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XXVI.—THE CONSTITUENTS OF PENNSYLVANIA, OHIO, AND CANADIAN PETROLEUM BETWEEN 150° AND 220°.[1]

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The conflicting statements published long ago, and still uncorrected, concerning the composition of the portions of Pennsylvania petroleum distilling at 150°, the absence of any information relating to the constituents of Ohio and Canadian petroleum, and the erroneous assumptions as to the composition of American petroleum based on the results of Markownikoff and his assistants in the Russian oil, taken together, render a study of these portions of American petroleum of extreme interest. One cannot fail to be impressed with the marked differences of opinion that have prevailed as to the composition of the portions of American petroleum with higher boiling-points. Some authorities, influenced by the profound investigations of the Russian chemists on the Caucasus oil, have believed that the constituents of American oil above 150° are naphtenes, with a reservation as to whether the series $C_n H_{2n}$, announced by Warren, should be accepted as naphtenes. Others, depending on the results of Pelouze and Cahours, which form the basis of the statements in chemical

1 Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Original Research.

literature concerning the constituents of Pennsylvania petroleum, have held that the series $C_n H_{2n+2}$ does not find its last representative in nonane (boiling-point 151°). Similar differences of opinion have been expressed by practical oil men, those who have witnessed the development of the petroleum industry from the beginning, concerning the composition of these oils. Some believe that Canadian and Ohio oils are esentially and fundamentally different from the Pennsylvania oil. Others hold that the chief constituents are identical, and that differences observed in refining are due to variations in the proportions of the principal constituents, and to the presence in certain oils of small amounts of other bodies that are not found in all. I must admit that my earlier impressions on this subject have not been verified in the light of the results which will be presented. This work was undertaken with the expectation that Pennsylvania oil would prove to consist in its higher portions of a series $C_n H_{2n}$, and it is only after a great amount of laborious study, and a vast accumulation of analytical data, presenting unquestionable evidence that, for the hydrocarbons distilling within these limits of temperature, except those collecting at 196° and 216° from Canadian petroleum, this series must be discarded—that I accept this conclusion. Concerning the composition of Ohio and Canadian petroleum, in the beginning of this work, I had no preconceived ideas.

The separation of constituents with higher boiling-points presents greater difficulties than of those in the portions distilling below 150°. In the lower portions there is no danger of decomposition during distillation, both on account of greater stability of the hydrocarbons and because the unstable bodies, such as the nitrogen, oxygen, and sulphur compounds, as well as the more complex hydrocarbons, distil for the most part at higher temperatures. Then distillation in air has little if any effect on the lower constituents, while the portions distilling at higher temperatures cannot be volatilized in the presence of air without more or less decomposition. As has been shown, distillation *in vacuo* prevents changes due to inherent instability, and it excludes air, but it increases very much the labor of the separations. It has been found to be

especially serviceable in separating the hydrocarbons under consideration, since these bodies are contained for the most part in portions of the first distillate boiling above the limits of cracking, and are consequently contaminated by the products of decomposition when distilled in air, and the decomposition-products are difficult to remove. Evidently any experiments on a laboratory scale may fail to reveal the presence of bodies that are present in proportionately minute quantities. It would be interesting, and from a commercial point of view doubtless profitable, to establish a more extended investigation involving the manipulation of at least a hundred barrels of crude oil, continuing the fractional separations of all portions until the individual hydrocarbons were as perfectly isolated as is done with smaller quantities in the laboratory. Such an investigation could only be undertaken at large expense, and a long time would be required to reach desirable results.

In undertaking this subject, the course to be followed was plain. There is but one method for the separation of these hydrocarbons, and it yields satisfactory results only after long and tedious application. Concerning the question as to whether fractional distillation can be relied on for the separation of hydrocarbons with boiling-points not far removed, it can, I think, be stated with confidence that distillations many times repeated under constant conditions may be expected to yield products whose composition can be determined, after suitable purification, as accurately as the methods of analysis will permit. But hydrocarbons separated from petroleum in this manner, before purification, may be contaminated by other bodies whose boiling-points are nearly the same. As an illustration, to ascertain whether Ohio petroleum contains a hydrocarbon boiling at 162°, a course of fractional separations under 730 mm. was repeated fifty times, forty-five times within one degree. One portion after treatment with fuming sulphuric acid had its specific gravity changed from 0.7717 to 0.7535, but it still distilled within the same limits. Another portion of the same distillate, after treatment with common concentrated sulphuric acid, gave a product with the same specific gravity and the same boiling-point as the oil before

treatment. The crude distillate contained a certain amount of mesitylene (boiling-point 163°) sufficient, as will appear later, to affect seriously the percentages of carbon and hydrogen. In the main, the hydrocarbons described in this paper as collecting between 160° and 216° have the same boiling-points as those described by Warren, except one which collected at 162°. It is peculiar that these bodies have nearly the same boiling-points as the naphtenes separated by Markownikoff from the Russian oil. In previous investigations on these hydrocarbons, except those of Warren, evidently the course of distillation was not sufficiently extended to separate with any degree of purity the individual constituents. In the light of Warren's distillations and those here presented, it is evident that Pelouze and Cahours could not have carried their separations far enough to obtain individual products. Concerning the thoroughness of Warren's separations there can be no question. But the deficiency in his work on the hydrocarbons now under consideration was the result of the limited knowledge then prevailing concerning the general composition of petroleum. The aromatic hydrocarbons, the oxygen compounds, and the nitrogen compounds, were not then recognized, or were merely suspected as constituents of petroleum. In the purification of his distillates, the single method adopted by Warren consisted in boiling with sodium, as shown by the following statement: "I must state, however, once for all, that, unless specially mentioned, no one of the bodies operated upon had received any chemical treatment except that of boiling with sodium."[1] But that Warren suspected the presence in his distillate of other bodies is indicated by a quotation from one of his private papers, already mentioned in another paper: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_2$, and $HONO_2$, and remove these."[2] It is evidently an error to consider the hydrocarbons $C_n H_{2n+2}$, especially the lower members, as unstable toward reagents. It has been our experience, in removing aromatic hydrocarbons from the distillate 160°–216°, that the principal constituents are not affected in the cold by

[1] Proc. Amer. Acad., **27**, 66. [2] This JOURNAL, **17**, 745.

a mixture of nitric and sulphuric acids, nor by fuming sulphuric acid even on warming. After purification, the boiling-points do not change in a long course of distillations. No doubt the stability diminishes with a rise in boiling-points, but it is sufficient to permit of purification of the members below 216°. All analyses in this paper point to the general composition $C_n H_{2n+2}$, except for the Canadian hydrocarbons 196° and 216°. If continued distillation or treatment with the means of purification we have adopted produces decomposition, the product should scarcely consist at least entirely of lower members of the same series.

In the comparative examination, the results of which will be described in this paper, two principal objects were kept in view: one of chief importance, to determine the series of hydrocarbons which form the main body of American petroleum, and the other naturally following, to ascertain whether the composition of Pennsylvania, Ohio, and Canadian oils as regards their principal constituents is the same.

In undertaking a study of the portions of petroleum within the limits of temperature mentioned above, it was at first determined to prepare all distillates from the crude oils, and this has been done in part in the Ohio and Canadian oils. But when it was found that cracking in refining did not begin to any considerable extent below 225°, and that distillates from the refinery resembled in all respects, at least in their principal constituents, those obtained in vacuum-distillation, refinery distillates were more freely employed, especially from Pennsylvania oil. But most of the results on Ohio and Canadian oils were obtained in vacuum-distillates, the preparation of which was described in a former paper.[1] Further assurance against decomposition in the Pennsylvania product was gained by selecting during the "run" in the refinery distillation just that portion of the distillates that corresponds in gravity to the constituents desired. Experience showed that heavier portions of the crude distillate should be selected than those corresponding to the constituents required, since the boiling-points invariably decline many degrees in subsequent distillations.

[1] Proc. Amer. Acad., 31, 1; This JOURNAL, 17, 713.

The refinery distillate employed was taken at 48°–50° Baumé, having a specific gravity of 0.7892 at 20°. It was very nearly colorless and gave no odor of decomposition. Forty-five liters of this distillate was fractioned within limits of 10°, 5°, 2°, and for a long time within 1°. It gradually collected in heaps, as described by Warren, but the prolonged distillation was necessary to separate higher and lower constituents from the mixtures between.

Concerning the impression that Pennsylvania petroleum has the same composition between these limits as the Russian oil, which is based in part on the results of Warren suggesting the series C_nH_{2n}, and in part on the erroneous statements of Höfer, that Markownikoff found the same series in Pennsylvania that he had reported in Russian oil, it may be stated once for all that this identity is clearly excluded by the great difference in specific gravity of the corresponding distillates, without reference to the differences in percentage composition. These differences in composition are indicated at the outset by great differences in specific gravity of crude distillates at 16°, as shown by Markownikoff and Oglobine.[1]

	Baku.	American.
150°–200°	0.786	0.757
200°–250°	0.824	0.788
250°–320°	0.681	0.809

The same differences appear between the individual constituents :[2]

Baku naphtenes		B. P.	Specific gravity.
Dekanaphtene	$C_{10}H_{20}$	160°–162°	0.795 (0°)
Endekanaphtene	$C_{11}H_{22}$	180°–185°	0.8119 (0°)
Dodekanaphtene	$C_{12}H_{24}$	196°–197°	0.8055 (14°)

—and the series C_nH_{2n} of Warren, purified only by distillation and boiling with sodium :[3]

		B. P.	Specific gravity at 0°.
Rutylene	$C_{10}H_{20}$	174°.9	0.7703
Margarylene	$C_{11}H_{22}$	195°.8	0.7822
Laurylene	$C_{12}H_{24}$	216°.2	0.7905

As will be shown later, the specific gravity assigned by Warren to these constituents is very materially diminished by

[1] Ber. d. chem. Ges., **16**, 1873. [2] *Ibid.*, 1877.
[3] Proc. Amer. Acad., **27**, 15.

the removal of the aromatic hydrocarbons, and perhaps of other heavier bodies, that can only be separated by the application of more vigorous means of purification than Warren applied.

Decane, $C_{10}H_{22}$, 163°–164°.

When Pelouze and Cahours announced that the hydrocarbon $C_{10}H_{22}$ is a constituent of Pennsylvania petroleum boiling at 160° ("sensiblement"), the presence in petroleum of the aromatic hydrocarbons had not been demonstrated, and since treatment with concentrated sulphuric acid and carbonate of soda was the sole means of purification, it is evident that their product must have still contained mesitylene (boiling-point 163°), which, according to Engler, is contained in petroleum to the extent of 0.2 per cent. Then the specific gravity, 0.757 at 15°, assigned by them, is somewhat higher than that of this decane with mesitylene entirely removed. Warren did not observe the collection of a distillate at this point in any considerable quantity. But if, as it seems probable, Pelouze and Cahours investigated, not Pennsylvania, but Canadian petroleum, the close agreement between their specific gravity of decane at 160° with ours in Canadian petroleum is explained. In attempting to ascertain whether a hydrocarbon with this boiling-point is present in Pennsylvania petroleum in any considerable amount, the distillates 150°–170° were carried through a long series of distillations, until several hundred grams collected between 158° and 162° under 730 mm., and finally more than 100 grams between 162° and 163° under 760 mm. One portion of this distillate was dried over sodium for analysis.

0.1453 gram of the oil gave 0.4560 gram CO_2, and 0.1865 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Calculated for $C_{10}H_{30}$.	Found.
C	84.51	85.71	85.58
H	14.49	14.29	14.27

A determination of the specific gravity of this oil at 20° gave 0.7684. Its vapor-density was determined by the Hofmann method in the vapor of aniline.

0.1327 gram of the oil gave 66.8 cc. of vapor at 182°, under a tension of 373.2 mm.

II. 0.1113 gram of the oil gave 59.5 cc. of vapor at 182°, under a tension of 354.7 mm.

Calculated for $C_{10}H_{22}$.	Found. I.	Found. II.
4.92	5.21	5.16

A portion of the same distillate was treated with fuming sulphuric acid with the aid of heat, and occasional agitation. When first added, a slight rise in temperature was observed, doubtless caused by the formation of mesitylenesulphonic acid. The acid was diluted, neutralized with baric carbonate, and the filtered solution evaporated nearly to dryness. A barium salt separated in clusters of needles, sparingly soluble in cold, more so in hot water. The quantity of this salt was too small for analysis. Another portion of the same distillate with a mixture of nitric and sulphuric acids in the cold formed an oily layer above the acids, which became solid on standing, and after crystallization from hot alcohol the needles that separated melted at 83°–84°, the melting-point of dinitromesitylene being 86°. When the dinitro product was warmed with fuming nitric acid, it formed prisms sparingly soluble in alcohol, and melting at 225° (melting-point of trinitromesitylene, 230°). In the treatment with acids, 16 grams of the crude distillate gave 8 grams of the purified oil, with a loss of 50 per cent. When treated with fuming sulphuric acid, 16 grams of the crude product gave 9.5 grams of the pure oil, with a loss of 40 per cent. Mesitylene formed, therefore, a considerable proportion of the crude distillate. The purified oil had the faint odor characteristic of pure petroleum hydrocarbons. After the removal of the hygroscopic moisture, the oil had no effect on bright metallic sodium. It gave upon analysis values required for decane :

0.1644 gram of the oil gave 0.5084 gram CO_2, and 0.2284 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.34
H	15.49	15.44

The specific gravity of the purified oil at 20° was 0.7479, a

value somewhat lower, as mentioned above, than that formed by Pelouze and Cahours.[1]

Its vapor-density was determined by the Hofmann method. 0.1221 gram of the oil gave 68.5 cc. of vapor at 182°, and under a tension of 352.8 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.91	4.91

Although the composition as shown by analysis seemed to be sufficient to demonstrate the presence of a hydrocarbon at this point, evidently analytical data alone would be insufficient, unless supported by a constant boiling-point. The distillate used in the determination described above was obtained after a long fractional separation, but without purification, except the removal of sulphur compounds, until after the distillations were made. To prove beyond question the constancy in boiling-point, another portion of the crude distillate after the fifteenth distillation was thoroughly agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued fourteen times longer. About 100 grams of the oil collected so that it distilled at 163°–164°, mostly at 164°, under a tension of 760 mm., and with the mercury column all in the vapor. There seems, therefore, to be no reasonable doubt that Pennsylvania petroleum contains a decane with this boiling-point. That this hydrocarbon is a decane is shown also by a determination of its molecular weight by the Beckmann method, which gave 142; and the formula $C_{10}H_{22}$ requires 142.

In forming the chlorine derivative of the hydrocarbon $C_{10}H_{22}$ (boiling-point 163°–164°) from Pennsylvania petroleum 45 grams of the purified hydrocarbon was subjected to the action of chlorine in sunlight with a sheet of paper interposed, until it increased in weight 17 grams. The chlorine was delivered rapidly above the oil, and it was absorbed as fast as it could be added. Hydrochloric acid escaped with effervescence, and the rapidity of the reaction generated sufficient heat to maintain the temperature in the vicinity of 70°. With a slower stream of chlorine in other experiments the heat was dissipated without heating the oil, although the chlorine was

[1] Ann. chim. phys. [4], 1, 62.

as readily absorbed. Without further treatment, the chlorine product was subjected to fractional distillation *in vacuo* under tension of 80 mm. After ten distillations, approximately 6 grams collected at 125°–130°, which determinations of chlorine, carbon and hydrogen showed to be monochlordecane:

I. 0.2181 gram of the oil gave 0.5460 gram CO_2, and 0.2265 gram H_2O.

II. 0.2024 gram of the oil gave 0.1660 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	68.23	....
H	11.90	11.55	....
Cl	20.11	....	20.29

The specific gravity of this chlordecane at 20° was 0.8914. The specific gravity of the same product, separated by Pelouze and Cahours, was not given. The chlordecanaphtene prepared by Markownikoff and Oglobine,[1] from decanaphtene boiling at 160°–162°, had the specific gravity 0.9390 at 0°. It boiled at 205°–206° (cor.). Chlordecane obtained by Pelouze and Cahours boiled under atmospheric pressure at 200°–204°. Our chlordecane could not be distilled under atmospheric pressure without decomposition. As nearly as its boiling-point could be determined, it distilled at 197°–203°.

On account of the small quantity of the chlorine derivatives described in this paper, the specific-gravity determinations may not be strictly accurate. But the errors are doubtless small, and they do not affect the value of the determinations in establishing the identity of these derivatives.

In continuing the distillation of the higher chlorinated products from the decane (boiling-point 163°–164°) of Pennsylvania petroleum, approximately 15 cc. of an oil collected after the eighth distillation, at 160°-170°, that was heavier than water. Even these high distillates, which could not be heated to their boiling-points without decomposition, could be distilled *in vacuo* with little, if any, decomposition. This product gave, on analysis, the values required for dichlordecane:

I. 0.2293 gram of the oil gave 0.4829 gram CO_2, and 0.1884 gram H_2O.

II. 0.2557 gram of the oil gave 0.3420 gram AgCl.

[1] Ann. chim. phys. [6], **2**, 453.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	Found. II.
C	56.87	57.42	....
H	9.48	9.13	....
Cl	33.65	....	33.09

This dichlordecane gave 1.0187 as its specific gravity at 20°.

Decane, $C_{10}H_{22}$, 173°–174°.

Above 163° (730 mm.) the distillates were small in amounts to 168°, where they began to increase, and large quantities collected within degree limits to 173°, when they again fell off to small volumes. The fraction 169°–170° was selected for examination, which included analyses of the crude distillate, analyses after purification with acids, and the formation of the chlorine derivatives. It is interesting to note that unpurified distillates give percentages of carbon and hydrogen corresponding to the series C_nH_{2n}, or to numbers between this series and the series C_nH_{2n+2}. The unpurified distillate 169°–170° (730 mm.) gave the following results:

0.1521 gram of the oil gave 0.4758 gram CO_2, and 0.2018 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Calculated for $C_{10}H_{20}$.	Found.
C	84.51	85.71	85.31
H	15.49	14.29	14.72

The specific gravity of this distillate at 20° was found to be 0.7502. Its vapor-density, determined by the Hofmann method, gave the following value:

0.1533 gram of the oil gave 74.6 cc. of vapor at 182°, under a tension of 414.6 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.86

Evidently no particular value can be attached to such determinations of vapor-density, since, as shown by analysis, the oil is not composed of a single body. The same is true of boiling-points unsupported by other values. The contaminating body frequently has the same or nearly the same boiling-point as the principal constituent, and after the removal of the impurity the boiling-point is not materially changed. Another portion of the crude distillate was shaken with ordi-

nary strong sulphuric acid, washed with caustic soda, water, and dried with sodium.

I. 0.1476 gram of this oil gave 0.4586 gram CO_2, and 0.1980 gram H_2O.

II. 0.1674 gram of this oil gave 0.5190 gram CO_2, and 0.2263 gram H_2O.

	I.	II.
C	84.72	84.57
H	14.90	15.03

The specific gravity of this oil was 0.7486. Its vapor-density was determined: 0.1454 gram of the oil gave 73 cc. of vapor at 182°, under a tension of 410 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.75

Another portion of the crude distillate was agitated with a mixture of nitric and sulphuric acids. An oily nitro product separated above the acids, which became partially crystalline on standing. It was doubtless a nitro derivative of cymol (boiling-point of metacymol 174°–176°, of paracymol 171°–172°).

The quantity of the nitro product was small, and the proportion of cymol was still further shown to be very small by treatment with fuming sulphuric acid. 185 grams of the distillates 167°–170°, after the eighteenth distillation, first by agitation in the cold, and then by warming to 125°, gave a loss in weight of only 15 grams, or about 8 per cent. of the weight taken. A barium salt was formed of the sulphonic acid, but it appeared as a thick gummy mass, so uninviting that nothing further was done with it. The purification with fuming sulphuric acid was intended more especially to show whether the boiling-point of the distillates would be materially affected. But the only difference observed was that they came together more readily and completely within one degree, 169°–170°, under 730 mm., and at 173°–174°, chiefly at 174°, under a tension of 760 mm., with the mercury column all in the vapor. It is interesting to observe how slightly the boiling-point was affected by the removal of the contaminating bodies. Evidently, the principal influence of the latter

was in preventing the hydrocarbon from collecting closely at its true boiling-point.

The remaining oil was boiled with sodium as long as the metal was affected, and until it remained unchanged on standing with the oil. Even after this treatment was repeated several times, the percentage of carbon was somewhat too high and of hydrogen too low.

0.1503 gram of the oil gave 0.4664 gram CO_2, and 0.2050 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.65
H	15.49	15.14

After this purification the specific gravity obtained was 0.7475. For still further certainty as to the purity and composition of this distillate another portion was warmed during several hours with fuming sulphuric acid and shaken thoroughly. After washing and standing over sodium it was analyzed:

0.1754 gram of the oil gave 0.5431 gram CO_2, and 0.2442 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.45
H	15.49	15.47

In the latter treatment the acid solution, when neutralized with baric carbonate, gave a barium salt in clusters of needles, sparingly soluble in water, doubtless the barium salt of cymolsulphonic acid, although the quantity obtained was too small for analysis.

After this prolonged treatment with the fuming acid, the specific gravity was found to be 0.7467, substantially the same as in the previous determinations, and practically the same as the specific gravity of the decane boiling at 163°.

The molecular weight of this hydrocarbon, as determined by the Beckmann method, using benzol as a solvent, was found to be 144; since the formula $C_{10}H_{22}$ requires 142, this determination leaves no doubt that this body is decane, and not a higher homologue.

The chlorine derivatives of the decane boiling at 173°–174° were formed in the same manner as those of its isomer. 32

grams of the purified distillate was allowed to absorb 9 grams of chlorine, and the product was fractioned *in vacuo*. After the fourth distillation a small quantity collected at 130°–140°, which gave the percentages of carbon, hydrogen, and chlorine required for monochlordecane.

I. 0.2082 gram of the product gave 0.1699 gram AgCl.

II. 0.2003 gram of the product gave 0.5038 gram CO_2, and 0.2150 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	....	68.61
H	11.90	....	11.93
Cl	20.11	20.19	....

The specific gravity of this chlordecane at 20° was 0.8874, a value somewhat lower than the specific gravity of the chlordecane formed from the decane boiling at 163°, *viz.*, 0.8914. After the study of its other properties not enough of this chlordecane remained for a determination of its boiling-point under atmospheric pressure. As the specific gravity of the chlorine derivative of petroleum decane, Lemoine[1] gave 0.908. This value must have been obtained from decane boiling at 162°, since the French chemists have never recognized a decane in petroleum boiling at 173°. It was probably obtained in an impure product, since it is very considerably higher than our determination, which was made, as already shown, in chlordecane from well purified decane.

In continuing the vacuum-distillation of the chlorine products from the decane boiling at 173°, a considerable quantity collected at 170°–171°, 80 mm., which distilled at 235°–240°, 747 mm. Its composition was shown by analysis.

0.2008 gram of the oil gave 0.4121 gram CO_2, and 0.1641 gram H_2O.

0.2540 gram of the oil gave 0.3532 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	55.96	....
H	9.48	9.08	....
Cl	33.65	....	34.38

This substance is, therefore, dichlordecane. The quantity

[1] Bull. Soc. chim., (Paris), 41, 165.

obtained was barely sufficient for a determination of its specific gravity ; it gave at 20°, 1.0126.

The presence of a decane at 174° seems therefore to be established in Pennsylvania petroleum, confirming the observations of Warren, who alone of all those who have examined American petroleum found a body at this point. If Pelouze and Cahours had carried their course of distillations sufficiently far, they could not have failed to discover this body, since it forms such a large proportion of the higher boiling petroleum distillate. Those chemists did, however, collect a distillate at 180°-182°, which gave analytical values and a vapor-density very closely supporting the formula $C_{11}H_{24}$. For some time I was in doubt as to whether a distillate might not persist at this point, and it was only after a prolonged series of separations that it was possible to separate the distillates, 180°–182°, entirely into higher and lower limits, thus supporting the conclusion of Warren, that Pennsylvania petroleum contains no hydrocarbon in appreciable quantity boiling in the vicinity of 180°.

Hendecane, $C_{11}H_{24}$, 196°.

As the boiling-point rose, the distillates showed less stability, as indicated by more color in the residue in a long course of distillations, although this was not sufficient to interfere with the collection of a homogeneous body within narrow limits of temperature. Between 189° and 192° distillates early began to accumulate, and the quantity gradually increased until 150 cc. was obtained, which distilled entirely at 190°–191, under 730 mm.

On standing over sodium, a portion of this distillate deposited a reddish flocculent precipitate in very appreciable quantity, which indeed was observed in all unpurified distillates. On this account very little importance has been attached to the composition of these oils, as shown by analysis, except to demonstrate what slight weight can be given to those results. Drying with sodium is indispensable, on account, as shown in another connection, of the difficulty in removing water by other means.

Determinations of carbon and hydrogen in the crude distil-

late. 190°–191°, dried over sodium, gave the following results:

0.1521 gram of the oil gave 0.4787 gram CO_2, and 0.1972 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.82
H	14.29	14.41

The specific gravity at 20° was found to be 0.7673. After thorough agitation with sulphuric acid and washing with sodic hydrate and water, the specific gravity was scarcely affected, 0.7662.

A comparison of the composition and specific gravity of the crude distillate, 190°–191°, 730 mm., as shown above, with the results of Warren and those of Pelouze and Cahours, in connection with what follows after further purification, reveals the cause of the lack of uniformity in the earlier work. The specific gravity of Warren's analyzed product, 0.7721 at 15°, which was only purified by boiling with sodium, is substantially the same as that of Pelouze and Cahours, 0.7780 at 20°, which was purified with concentrated sulphuric acid and sodic carbonate, but appreciably higher than the specific gravity of our crude distillate, only dried over sodium. The percentage-composition of these products purified in this manner may be more clearly understood if the results of analysis are brought together, as in the following table:

	Warren.		Mabery.	Pelouze and Cahours.	
	I.	II.		I.	II.
C	85.60	85.33	85.82	84.79	84.58
H	14.80	14.65	14.41	15.42	15.36

Required for

	$C_{11}H_{22}$.	$C_{11}H_{24}$.	$C_{12}H_{24}$.
C	85.72	84.62	84.70
H	14.29	15.38	15.30

It is difficult to see how results so closely supporting the formula C_nH_{2n+2} as those of Pelouze and Cahours could be obtained in a product still containing aromatic hydrocarbons, as shown by their method of purification and by the higher specific gravity. In the case of this particular hydrocarbon, the method of purification is not especially mentioned, but their general method, which is mentioned under nearly every

other member of the long series of hydrocarbons which they examined, consisted in agitating the oil in the cold with concentrated sulphuric acid and washing with sodic carbonate. Then their method included no special means of drying the oil for analysis. It is quite impossible to remove moisture entirely from these hygroscopic oils without the aid of the most vigorous desiccating agents. Nothing less than standing continuously over sodium, in my experience, will insure a perfectly dry condition.

It is evident from the following description of their experiments that Pelouze and Cahours tried the action of reagents on their oil, although they seem not to have suspected the presence of an aromatic hydrocarbon C_nH_{2n-6}: "Le brome, l'acide azotique fumant, l'acide sulfurique au maximum de concentration et l'acide azotique de Nordhausen ne l'attaquent pas à froid. Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition. Prolonge-t-on l'action, on voit se former une petite quantité d'un produit solide et crystallisable. Il se sépare en même temps une huile jaunâtre un peu plus dense que l'eau. De plus, on dèmêle dans les vapeurs nitreuses l'odeur caractéristique des acides volatils homologues de l'acide acétique."

Upon agitation with nitric and sulphuric acids, the distillate 190°–191° deposited a heavy nitro compound.

Our observations concerning the action of a mixture of concentrated nitric and sulphuric acids in the cold on this distillate do not coincide with those of Pelouze and Cahours. Immediately, upon vigorous agitation, a heavy nitro compound separated as a heavy oil, forming a crystalline product on standing. 20 grams of the oil lost 4.5 grams by this treatment, equivalent to 22 per cent. of its weight. The nitro compound was very sparingly soluble in hot alcohol, from which it crystallized in needles, melting at 169°–170°. As will be seen later, nitro compounds with the same melting-points were separated from Ohio and Canadian petroleum, which do not correspond in melting-point to that of either dinitrodurol, 205°, nor of dinitroisodurol, 156°, although crystallization was continued until the melting-point was pretty

constant. It would have been interesting to obtain sufficient of this substance for more complete examination; but, with the great amount of work on hand in connection with the principal hydrocarbons, it did not seem best to allow our attention to be diverted from the main object in view. It should not be understood that the diminution in weight mentioned above, on treating with acids, was due entirely to the removal of aromatic hydrocarbons. In all the petroleum hydrocarbons we have separated, on treating with nitric and sulphuric acids, a large proportion of the products has remained in solution, and it has been possible to reduce them only very slowly by heating with sodium. From the distillates above 150°, heavy dark brown precipitates have been formed at first, followed by light flocculent deposits resembling aluminic hydrate. On distilling after treating with sodium, usually a considerable residue is left. If heating with sodium be continued until there is no further action, the metal will remain bright in the oil, and we have looked on this as an indication of purity.

The oil separated from the acid mixture was boiled with sodium until it produced no further decomposition, shaken with sulphuric acid, and allowed to stand a long time in contact with sodium. Since the metal remained unaffected, the oil was assumed to be completely purified; nevertheless, analysis showed still remaining a trace of the less hydrogenized body:

0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.63	84.87
H	15.38	15.12

A determination of the specific gravity of the purified oil gave 0.7585.

To prove with greater certainty the composition of this hydrocarbon, the crude distillate obtained, as described above, was heated on the steam-bath with fuming sulphuric acid, which caused some decomposition, and the oil remaining washed thoroughly with caustic soda and water. 20 grams of the crude distillate gave 16.5 grams of the purified oil, with a

loss of 17.5 per cent., which is probably an approximate measure of the proportion of aromatic hydrocarbons in this distillate. It is probable that the loss in weight with the mixture of nitric and sulphuric acids included some decomposition of the principal hydrocarbon. The oil treated with fuming sulphuric acid was carried through ten distillations, after which it collected for the most part within one degree, and 100 grams distilled at 196°–197°, under 760 mm., and with the mercury column all in the vapor. This product was again warmed with fuming sulphuric acid, washed, and dried over sodium.

In the latter experiment the acid was only slightly discolored. The oil gave the faint characteristic odor of these hydrocarbons, which is easily recognized when the impurities are removed. It then gave percentages of carbon and hydrogen required for a hydrocarbon of the series $C_n H_{2n+2}$.

I. 0.1502 gram of the oil gave 0.4665 gram CO_2, and 0.2090 gram H_2O.

II. 0.1661 gram of the oil gave 0.5157 gram CO_2, and 0.2322 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.70	84.67
H	15.38	15.46	15.53

The specific gravity of the oil 196°–197°, after purification in this manner, was found to be 0.7581. The close agreement in specific gravity of the products after treatment with the mixture of nitric and sulphuric acids, and with fuming sulphuric acid, as well as the proportions of carbon and hydrogen, indicate that the oil was quite thoroughly purified.

That the formula of the purified hydrocarbon boiling at 196° is $C_{11}H_{24}$, and not the next higher homologue, receives further support by a determination of its molecular weight, in which Mr. Hudson obtained, by the Beckmann method, the value 157; required for $C_{11}H_{24}$, 156.

In the preparation of the chlorine derivatives of the hydrocarbon $C_{11}H_{24}$, (boiling-point 196°) of Pennsylvania petroleum, 40 grams of the oil was allowed to absorb 14 grams of chlorine and the chlorine product was fractioned *in vacuo*. After five

distillations, 10 cc. collected at 145°-150° (80 mm.), that distilled with decomposition at 225°–230°, bar. 747 mm. This product gave on analysis percentages of carbon, hydrogen, and chlorine required for $C_{11}H_{23}Cl$:

I. 0.2291 gram substance gave 0.1713 gram AgCl.

II. 0.1933 gram of the substance gave 0.4914 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	II.
C	69.29	....	69.30
H	12.07	....	11.91
Cl	18.13	18.49	....

The specific gravity of monochlorhendecane at 20° was found to be 0.8721. Pelouze and Cahours found that the hydrocarbon which they collected at 196°–200° absorbed chlorine at a gentle heat with the formation of a monochlor derivative that boiled at 242°–245° with a specific gravity of 0.9330 at 22°. These values are much in excess of the determinations given above. Our boiling-point under atmospheric pressure was only approximate, since the chlorine product was considerably decomposed at those temperatures. In the action of chlorine, the substitution proceeded with the greatest readiness as soon as the chlorine came in contact with the hydrocarbon. No heat was necessary, although, if the action proceeded rapidly, much heat was developed.

The composition of the product obtained by Pelouze and Cahours corresponds with the formula $C_{12}H_{25}Cl$, as shown by the following record of their analyses:

	Calculated for $C_{12}H_{25}Cl$.	Found.
C	70.41	70.34
H	12.23	12.37
Cl	17.36	17.53

In further support of the formula $C_{11}H_{23}Cl$, Mr. Hudson made a determination of the molecular weight of the chloride by the Beckmann method, using benzol as a solvent, in which he obtained 191; the formula $C_{11}H_{23}Cl$ requires 190.

Evidently a dichlorhendecane was also formed in the chlorination, since in the vacuum-distillation, about 5 cc. collected at 190°–200°, that gave a percentage of chlorine two per cent.

too low for the required value. But the quantity was too small to purify it sufficiently to give acceptable results.

Dodecane, $C_{12}H_{26}$, 214°–216°.

Above 193°, 730 mm., the fractions were very small to 208°, but between 208° and 210° much larger quantities collected, for the most part at 209° to 210°. Without further purification, except drying with sodium, the crude distillate was analyzed:

0.1392 gram of the oil gave 0.4355 gram CO_2, and 0.1845 gram H_2O.

	Calculated for CnH2n.	Found.
C	85.71	85.33
H	14.29	14.73

A determination of its specific gravity gave 0.7745. After treatment with concentrated sulphuric acid, the specific gravity was not changed—0.7744. Another portion of the crude distillate was shaken with nitric and sulphuric acids, and allowed to stand several hours. After separation from the small quantity of the heavy nitro product and the acid, the oil was boiled with sodium until there was no further action, and the metal remained unaffected on standing several weeks. The oily nitro product deposited a small quantity of crystals on standing, but not enough to purify for a determination of its melting-point.

Purified in this manner, this distillate gave the following results on analysis:

I. 0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.

II. 0.1474 gram of the oil gave 0.4562 gram CO_2, and 0.2017 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found. I.	Found. II.
C	84.72	84.87	84.41
H	15.28	15.12	15.21

Its specific gravity at 20° was found to be 0.7684.

Another portion of the crude fraction, 209°–210°, purified by thorough agitation and warming with fuming sulphuric acid, twice repeated, gave the following results on analysis:

0.1471 gram of the oil gave 0.4537 gram CO_2, and 0.2068 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	84.72	84.12
H	15.28	15.63

The specific gravity of the oil after treatment with the fuming acid was 0.7729, somewhat higher than the portion purified with nitric and sulphuric acids. It is quite possible that the purification with fuming sulphuric acid, in this instance, was not capable of removing the contaminating bodies as thoroughly as the other method. The purified hydrocarbon was found to distil completely at 214°–216°, under a tension of 760 mm., and with the mercury column all in the vapor. A determination of its molecular weight by the Beckmann method gave Mr. Hudson 173; required for the formula $C_{12}H_{24}$, 170.

In the formation of the chlorine derivatives from the hydrocarbon $C_{12}H_{24}$, Pennsylvania petroleum, 95 grams of the purified hydrocarbon was exposed to the action of chlorine until 30 grams was absorbed. Apparently chlorine substitutes as readily in the hydrocarbons of higher, as in those of lower, boiling-points. In fractioning under 80 mm. after six distillations, about 20 cc. collected at 142°–153°, which distilled at 230°–235° atmospheric pressure. In none of the distillates of chlorine derivatives was hydrochloric acid detected as a product of decomposition when distilled *in vacuo*. Under atmospheric pressure it was impossible to carry on these distillations without serious decomposition. The composition of this fraction corresponded to that of $C_{12}H_{23}Cl$.

I. 0.1910 gram of the oil gave 0.1385 gram AgCl.

II. 0.1339 gram of the oil gave 0.3434 gram CO_2, and 0.1423 gram H_2O.

	Calculated for $C_{12}H_{23}Cl$.	Found. I.	Found. II.
C	70.42	....	69.93
H	12.23	....	11.81
Cl	17.36	17.93	....

In determining the specific gravity of this chlorine derivative at 20° it gave 0.8919. A determination of its molecular

weight by the Beckmann method, with benzol as a solvent, gave Mr. Hudson 200; required for $C_{13}H_{25}Cl$, 204. The chloride formed by Pelouze and Cahours from their distillate 216°–218° boiled at 258°–260°, somewhat higher than the boiling-point of their chloride described in this paper. From the results of their analyses, they deduced the formula $C_{13}H_{27}Cl$.

The chlorination of this product was not carried far enough to form sufficient of the dichlor derivative to separate it by distillation. The greater part of the oil after chlorination distilled at 212°–214°, the boiling-point of the hydrocarbon.

A description of these experiments, which are intended to establish the composition of the hydrocarbon distilling at 214°–216°, should not be concluded without a statement of the relation they sustain to those of Warren and of Pelouze and Cahours, the only experimenters who have hitherto attempted the separation of this constituent from American petroleum. The two determinations most nearly concerned in this discussion are specific gravity and percentage composition. In the following comparison of specific-gravity determinations and percentage composition, it should be borne in mind that Warren purified his distillate only by boiling with metallic sodium, Pelouze and Cahours by agitation with concentrated sulphuric acid and washing with sodic carbonate; with those results are brought together the determinations described in this paper in the crude distillate, after agitation with concentrated sulphuric acid, and after more thorough purification with the acid mixture:

	Warren, 15°.		Pelouze and Cahours, 20°.		Crude distillate.	Mabery. 20°. Agitation with H_2SO_4.	Purified.	
Sp. gr.	0.7804		0.7960		0.7745	0.7744	0.7684	
	I.	II.	I.	II.			I.	II.
C	84.66	85.74	84.58	84.51	85.33		84.87	84.41
H	14.85	14.66	15.37	15.45	14.73		15.12	15.21

The percentages of carbon and hydrogen required for the formula $C_{13}H_{26}$ are: C, 84.72; H, 15.30; for the formula $C_{13}H_{28}$: C, 84.78; H, 15.22. Evidently the differences in percentage-composition are not sufficient to determine by analysis alone which of the two formulas is the correct one. But the differences between either of these formulas

and the formula $C_{12}H_{24}$ (C, 85.71; H, 14.29) should be readily shown by analysis.

Having at hand a portion of the purified distillate (214°–216°) that had been treated with chlorine and the part not chlorinated distilled, I continued the distillation until the chlorine derivatives were completely removed, and the hydrocarbon was then treated with fuming sulphuric acid and distilled over sodium. It then gave as its specific gravity 0.7749, substantially the same as before chlorination. Normal dihexyl prepared by the action of zinc and hydrochloric acid on normal hexyl iodide boils at 214°.5 and apparently is identical with a hydrocarbon having the same composition, obtained by electrolysis of potassium œnanthylate (Schorlemmer). The latter has the specific gravity 0.7738 at 17°. It is therefore probable that the hydrocarbon $C_{12}H_{26}$, boiling at 214°–216°, from American petroleum, has the same form. The purified hydrocarbon then gave the following percentages of carbon and hydrogen:

I. 0.1599 gram of the oil gave 0.4978 gram CO_2, and 0.2177 gram H_2O.

II. 0.1617 gram of the oil gave 0.5021 gram CO_2, and 0.2270 gram H_2O.

III. 0.1559 gram of the oil gave 0.2193 gram H_2O. The CO_2 was lost.

	Calculated for $C_{12}H_{26}$.	Found I.	Found II.	Found III.
C	84.72	84.89	84.69	....
H	15.28	15.10	15.31	15.63

The results indicate the absence of any impurity not readily acted on by chlorine.

As one of the results of this examination it can, I think, be safely asserted that the constituents of Pennsylvania petroleum with boiling-points at 163°–164°, 173°–174°, 196°–197°, and at 215°–216°, constitute the main body of this petroleum within these limits, and whatever other bodies may be present, they are to be found only in comparatively small quantities. As to the proportion of aromatic hydrocarbons in the crude oil, no direct estimation can be based on these observations.

Fuming sulphuric acid removed 40 per cent. of the crude distillate 160°–161°, leaving decane as the remaining 60 per cent. Whether the portion removed was mesitylene alone may be questionable, but no doubt it formed the larger part of the body uniting with the fuming acid. Even in such prolonged fractional separations as those described in this paper, it cannot be assumed that nearly all the decane 163°–164° was collected in the fractions which should contain it, neither is it probable that the crude distillate from which was selected the specimen for the separation of these constituents contained all the decane in the corresponding quantity of crude oil. But it is evident that the aromatic hydrocarbons are present in no inconsiderable amounts, and without doubt these bodies have much influence on the illuminating qualities of the oil. As shown by the slight changes in specific gravity after the action of ordinary concentrated sulphuric acid, the action of this acid in the usual method of refining does not include to any considerable extent the removal of the aromatic hydrocarbons. Its beneficial action seems to concern more especially the decomposition-products of distillation and certain constituents present in minute quantities, such as the unsaturated hydrocarbons, the oxygen, and nitrogen compounds. It scarcely need be mentioned that this applies to the action of sulphuric acid in the cold. When heated, without doubt a part of the aromatic hydrocarbons would be removed, to the detriment of the burning qualities. The formation of barium salts from all the distillates treated with fuming sulphuric acid proves the presence in appreciable amounts of a wide range of aromatic hydrocarbons.

Without reference to the percentages of carbon and hydrogen, the low specific gravity of the hydrocarbons described above is sufficient to show that they are not naphtenes. The following comparison of the unpurified distillates and the purified hydrocarbons as regards their specific gravity with the naphtenes separated by Markownikoff from the Russian oil will perhaps make these differences more clearly understood.

Baku naphtenes :

	B. P.	Specific gravity.
$C_{10}H_{20}$	160°–162°	0.795 (0°)
$C_{11}H_{22}$	180°–182°	0.8119 (0°)
$C_{12}H_{24}$	196°–197°	0.8055 (14°)

Pennsylvania hydrocarbons, $C_n H_{2n+2}$:

	B. P.	Specific gravity at 20°. Purified.	Unpurified.
$C_{10}H_{22}$	163°–164°	0.7479	0.7684
$C_{10}H_{22}$	173°–174°	0.7467	6.7502
$C_{11}H_{24}$	196°–197°	0.7381	0.7673
$C_{12}H_{26}$	214°–216°	0.7676	0.7745

Another important result of this study is the evidence that the main body of the hydrocarbons in Pennsylvania petroleum within these limits of temperature are members of the series $C_n H_{2n+2}$. Satisfactory analytical data in proof of this conclusion have cost a vast expenditure of time and effort, not only in the routine labor of separation and purification, but in obtaining sufficiently close percentages of carbon and hydrogen. In such a large number of determinations the ordinary method of combustion becomes exceedingly tedious, since all details must be watched with the greatest care. In the early part of the analytical work there was not the slightest evidence as to whether the hydrocarbons were of the series $C_n H_{2n+2}$, or of the series $C_n H_{2n}$. The extreme hygroscopic nature of these bodies was not then appreciated, nor the refinement in purification necessary to yield accurate results. Many analyses were made before these details were fully understood.

Constituents of Ohio Trenton Limestone Petroleum.

The constituents of Ohio petroleum between 160° and 216° were sought for in vacuum-distillates obtained from the crude oil, as described in a former paper.[1]

Distillation *in vacuo* was continued until all portions had collected that could be brought together within the desired limits. Further concentration was carried on under atmospheric pressure, since this did not occasion serious decomposition. Probably no petroleum distillates with such high boiling-points can entirely escape decomposition in a long

[1] This JOURNAL, 17, 739.

course of distillations, but small amounts of decomposition-products can no doubt be removed by sulphuric acid, leaving the main body of the oil free from contamination. After the first distillations *in vacuo*, Ohio distillates seem to suffer no more change during distillation than those from Pennsylvania oil. Before separation into two-degree fractions, the sulphur compounds were removed as far as possible by precipitation with mercuric chloride. As the distillations proceeded, the characteristic "heaps" began to appear in the vicinity of 160°, 730 mm., falling off below 158° and above 163°. These portions were therefore carried through a long course of separations, fifty altogether, forty-five within one degree, after which they collected mainly at 159°–162°. A combustion of the crude distillate 159°–160°, purified as explained above only by mercuric chloride, gave the following results:

I. 0.1591 gram of the oil gave 0.4983 gram CO_2, and 0.2076 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Calculated for $C_{10}H_{22}$.	Found.
C	85.71	84.51	85.41
H	14.29	15.49	14.50

On the basis of these values alone, there should be no hesitation in assigning to this oil the formula $C_{10}H_{20}$. The specific gravity of this distillate was found to be 0.7717. Its vapor-density was determined by the Hofmann method:

0.1272 gram of the oil gave 67 cc. of vapor at 182°, and under a tension of 374.4 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.96

After treatment with ordinary concentrated sulphuric acid, another portion of this distillate gave 0.7678 as its specific gravity, and the following percentages of carbon and hydrogen:

0.1416 gram of the oil gave 0.4452 gram CO_2, and 0.1855 gram H_2O.

C	85.76
H	14.56

Agitation of the crude distillate in the cold with a mixture of concentrated nitric and sulphuric acids caused the

separation of a heavy oil that deposited crystals of a nitro product on standing. After crystallization from hot alcohol, in which it is sparingly soluble, this substance melted at 229°, showing it to be trinitromesitylene (melting-point 230°–232°). Complete removal of the nitro compound from decane required prolonged boiling with sodium followed by agitation with sulphuric acid. The hydrocarbon then no longer attacked the metal, nor tarnished it on long standing. Purified in this manner, this oil gave values required for decane :

0.1512 gram of the oil gave 0.4677 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.35
H	15.49	15.35

For further assurance as to the composition of this hydrocarbon, another portion of the crude distillate was first agitated in the cold with fuming sulphuric acid, which produced no heat, and then heated with the acid on the steam-bath. As in most of the crude oils when treated in this manner, the acid turned dark when heated, and evidently extracted a considerable proportion of the oil. After washing with sodic hydrate and water, the remaining oil gave only the faint odor characteristic of the petroleum hydrocarbons. In many of the analyses it will be seen that the percentage of hydrogen is somewhat lower than is required by a pure substance. This deficiency is doubtless due to a very small proportion of the hydrocarbon with less hydrogen, the last traces of which it is somewhat difficult to remove. The fraction 160°–162°, after the last purification, contained the following percentages of carbon and hydrogen :

0.1532 gram of the oil gave 0.4740 gram CO_2, and 0.2113 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.38
H	15.49	15.33

A determination of its specific gravity at 20° gave 0.7535, a value slightly higher than the specific gravity of the corresponding fraction of the Pennsylvania oil, doubtless due to the

slight trace of impurity still remaining. In determining the molecular weight of this decane by the method of Beckmann, Mr. Hudson obtained 145; required for $C_{10}H_{22}$, 142.

The boiling-point of this hydrocarbon, so thoroughly purified that neither fuming nitric acid nor fuming sulphuric acid produced further change, was found to be nearly the same as that of the decane (boiling-point 163°) from Pennsylvania petroleum. 50 cc. distilled entirely between 162°.5 and 163°.5, under a barometric pressure of 757.5 mm.

Since even a larger proportion of the crude distillate was removed in combination with fuming sulphuric acid than from the Pennsylvania distillate, 163°, an attempt was made to ascertain the composition of the barium salt, formed by neutralizing with baric carbonate and crystallizing the filtered solution, after boiling with bone-black. A considerable quantity of the barium salt crystallizing in needles was obtained, and the percentage of barium found (25.95) agreed closely with the theoretical percentage of barium in barium mesitylenesulphonate, $(C_9H_{11}SO_3)_2Ba$ (25.61). But the salt proved to be anhydrous, while according to Jacobson[1] barium mesitylenesulphonate crystallizes with $9H_2O$. On account of the limited supply of the barium salt, it was not possible to verify this determination by further study; but there can be no doubt of the possibility of forming a barium salt of mesitylenesulphonic acid in this manner, since trinitromesitylene melting at 225°–230 (melting-point of trinitromesitylene, 230°) was formed without difficulty by the action of fuming nitric acid on this distillate.

As further evidence of the composition of the hydrocarbon, 163°, Ohio petroleum, 46 grams well purified with fuming sulphuric acid was exposed to the action of chlorine until the weight had increased 11 grams. The chlorinated product was fractioned twelve times under 80 mm., when 15 cc. collected at 130°–135°, distilling at 200°–208°, atmospheric pressure. It was shown by analysis to have the composition required for $C_{10}H_{21}Cl$.

I. 0.2340 gram of the substance gave 0.1934 gram AgCl.

[1] Ann. Chem. (Liebig), **146**, 98.

II. 0.1935 gram of the substance gave 0.4785 gram CO_2, and 0.2119 gram H_2O.

III. 0.1715 gram of the oil gave 0.4246 gram CO_2, and 0.1963 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00	....	67.44	67.53
H	11.90	....	12.17	12.73
Cl	20.11	20.45	....	....

In a determination of its specific gravity at 20°, this chlordecane gave 0.8958. In continuing the distillation of the chlorine product after the twelfth fraction, 10 cc. collected at 160°–170°, specific gravity 1.0627 at 20°, which gave the percentages of carbon, hydrogen, and chlorine required for $C_{10}H_{20}Cl_2$:

I. 0.2984 gram of the substance gave 0.4105 gram AgCl.

II. 0.2753 gram of the substance gave 0.5746 gram CO_2, and 0.2356 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	....	56.94
H	9.47	....	9.51
Cl	33.65	34.03	....

Normal Decane, B. P. 173°–174°.

Above 162° (730 mm.) the distillates were small to 168°. After long continued distillation, 300 grams collected at 169°–170° (730 mm.), which, without further purification, except drying over sodium, gave the following percentages of carbon and hydrogen:

I. 0.1434 gram of the oil gave 0.4486 gram CO_2, and 0.1927 gram H_2O.

II. 0.1577 gram of the oil gave 0.4948 gram CO_2, and 0.2070 gram H_2O.

	Calculated for $C_{10}H_{22}$.	$C_{10}H_{20}$.	Found. I.	II.
C	84.51	85.71	85.33	85.55
H	15.49	14.29	14.94	14.58

A determination of the specific gravity of this distillate gave 0.7621, a value considerably higher than that of the corresponding unpurified Pennsylvania distillate, 0.7502.

0.1670 gram of the oil gave 79 cc. of vapor at 182°, under a tension of 366 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.90	5.15

A portion of the crude distillate was shaken with concentrated sulphuric acid, washed, and dried for analysis:

0.1504 gram of the oil gave 0.4708 gram CO_2, and 0.1984 gram H_2O.

C	85.37
H	14.67

The specific gravity of this oil, after treatment with sulphuric acid, was somewhat lower than that of the crude distillate, 0.7580. A determination of its vapor-density gave 5.02. The fraction 169°–170°, Ohio oil, was the first to be submitted to the action of the mixture of nitric and sulphuric acids. When a small quantity of the oil was heated to about 125° during twenty-four hours with the acid mixture, nitrous fumes were freely evolved and the volume of the oil gradually diminished until very little remained. Upon diluting the acid, a heavy, tarry mass was precipitated, evidently a product of decomposition of the hydrocarbon. In another experiment, 24 grams of the crude distillate were agitated in the cold with the acid mixture, separated from the acid and the oily nitro product, washed, and dried. After boiling with sodium and shaking with sulphuric acid, there remained only 17 grams, there having been a loss of 32 per cent. A portion of the nitro product crystallized on standing, and after several crystallizations from hot alcohol, in which it was sparingly soluble, the melting-point could not be raised above 164°–165°. In testing the action of sulphuric acid alone on the distillate 171°–172°, 25 grams of the crude oil was agitated with three successive portions of concentrated sulphuric acid, washed with sodic hydrate and water, and dried. In the first treatment, in which the oil lost in weight 1.8 grams, the acid was badly discolored; the subsequent portions were not affected. The oil was next heated gently with fuming sulphuric acid with agitation, which caused considerable blackening, washed first with concentrated sulphuric acid, then with sodic hydrate

and water, and dried. After the last treatment, the oil weighed 19.8 grams, a loss of 25 per cent.

It is evident from these observations that some care is necessary in attempting to purify these hydrocarbons with concentrated nitric acid. In the cold or under a gentle heat, not prolonged, the decomposition is probably not serious. But at higher temperatures, as shown above, the action may proceed too far. The purified oil gave satisfactory results on analysis:

I. 0.1373 gram of the oil gave 0.4247 gram CO_2, and 0.1900 gram H_2O.

II. 0.1459 gram of the oil gave 0.4520 gram CO_2, and 0.2090 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	Found. II.
C	84.51	84.36	84.47
H	15.49	15.38	15.92

Two determinations of the specific gravity at 20° of this oil in different preparations gave 0.7519 and 0.7513.

In a still more extended purification, some of the crude distillate was agitated thoroughly with the mixture of nitric and sulphuric acids, allowed to stand several hours with the acids, and, after washing, heated for some time with tin and hydrochloric acid. The washed and dried oil was then warmed with fuming sulphuric acid, washed, dried, and distilled. It then gave 0.7482 as its specific gravity at 20°, more nearly approaching the specific gravity of the Pennsylvania decane, 173°, 0.7467, and analysis indicated that the remaining oil had the composition of the general formula C_nH_{2n+2}:

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

Another quantity of the crude distillate was heated on the steam-bath during several hours with fuming sulphuric acid, the acid being occasionally shaken with the oil, boiled with sodium, distilled, and dried for analysis:

0.1519 gram of the oil gave 0.4715 gram CO_2, and 0.2085 gram H_2O.

C	84.67
H	15.26

The specific gravity of this product was the same as before, 0.7514. In a determination of the molecular weight of the hydrocarbon purified by the mixture of nitric and sulphuric acids, tin and hydrochloric acid, fuming sulphuric acid, and sodium, Mr. Hudson obtained 142 ; required for $C_{10}H_{22}$, 142. The fuming sulphuric acid solution separated from the oil was neutralized with baric carbonate, filtered, and evaporated nearly to dryness. On cooling, a barium salt separated in needles, which were very sparingly soluble in cold water. The air-dried salt was anhydrous, and it gave, by ignition with sulphuric acid, 25.46 per cent. of barium. Hexahydrocymol requires 23.8 per cent. of barium, and isocymol 24.3. The first hydrocarbon boils at 171°–172°, *m*-cymol at 174°–176°, *p*-cymol at 172°–173°, and pseudocymol at 169°. By fuming sulphuric acid at least the isocymol, if present in petroleum, should be extracted, and it is probable that this barium salt was an impure compound of cymolsulphonic acid. That the decane boiling at 174° is the principal constituent of Ohio petroleum at this point, and that it contains a considerable proportion of aromatic hydrocarbons, has received ample proof. As to the precise form of the aromatic hydrocarbons, the quantity of material it has been expedient to manipulate in purifying the decane was not sufficient to demonstrate. It would evidently be impossible to separate these bodies from decane in any course of distillation, and it would require a large quantity of the crude distillate, although not so thoroughly distilled as the one prepared in this examination.

In still further evidence as to the formula of this hydrocarbon, the chlorine derivatives were prepared by the action of chlorine on a portion purified with the mixture of nitric and sulphuric acids and sodium. 83 grams of the hydrocarbon was allowed to absorb 30 grams of chlorine, the theoretical quantity for the mono derivative being 20 grams. As an illustration of the readiness with which substitution takes

place, in this experiment the stream of chlorine happened to be exceptionally vigorous, but it was completely absorbed from the beginning to the extent of five grams during the first ten minutes. Hydrochloric acid escaped from the oil with brisk effervescence, although the chlorine was delivered at some distance above the surface of the oil. This rapid substitution at low temperature is quite unlike the substitution of chlorine in decanaphtene observed by Markownikoff and Oglobine, as shown by the following statement :[1] "Lorsqu'on fait agir du chlore sec sur les vapeurs du décanaphtène en ébullition et sous l'influence de l'insolation directe, la réaction se fait lentement avec dégagement d'acide chlorhydrique et demande un très grand excès de chlore en comparaison de ce qu'il en faut d'après le calcul théorique." Yet in the residue of the hydrocarbon not acted on by chlorine, Markownikof and Oglobine found a somewhat lower percentage of carbon and a higher percentage of hydrogen, from which, together with a slightly lower specific gravity, 0.792, than decanaphtene, 0.896, they infer that "ces chiffres semblent indiquer la présence d'une quantité notable d'un hydrocarbure saturé." In accordance with my observations on all the hydrocarbons from Pennsylvania, Ohio, and Canadian oil which I have chlorinated, these bodies should be saturated long before the naphtenes, especially if the latter react slowly with chlorine at the boiling temperature.

In fractioning *in vacuo* under 80 mm. the chlorinated oil, after several distillations, about 8 cc. collected at 134°–136°, with a small proportion of unaffected hydrocarbon which came over at a lower temperature. Analyses of this product gave numbers corresponding to the composition of chlordecane:

I. 0.2773 gram of the oil gave 0.6977 gram CO_2 and 0.2886 gram H_2O.

II. 0.1623 gram of the oil gave 0.4085 gram CO_2, and 0.1679 gram H_2O.

III. 0.2117 gram of the oil gave 0.1707 gram AgCl.

[1] Ann. chim. phys. (6), 2, 453.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00	68.60	68.54	....
H	11.90	11.56	11.50	....
Cl	20.11	....	....	19.93

A determination of the specific gravity of this chlordecane at 20° gave 0.8895. Under atmospheric pressure it distilled with some decomposition at 205°–210°. Its molecular weight, determined by the Beckmann method, was found by Mr. Hudson to be 174; required for the formula $C_{10}H_{21}Cl$, 176.5.

In continuing the fractional distillation *in vacuo* of the chlorine product from Ohio decane (boiling-point 173°) a small quantity, 3 cc., collected at 170°–180°, 80 mm., which distilled under atmospheric pressure at 240°–243°. On account of decomposition this portion was fractioned only five times, but it gave on analysis a percentage of chlorine corresponding to dichlordecane:

I. 0.2690 gram of the oil gave 0.5549 gram CO_2, and 0.2191 gram H_2O.

II. 0.2753 gram of the oil gave 0.5746 gram CO_2, and 0.2111 gram H_2O.

III. 0.3147 gram of the oil gave 0.4256 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.	III.
C	56.87	56.24	56.94	....
H	9.48	9.04	8.51	....
Cl	33.65	....	....	33.46

A determination of the specific gravity of this dichlordecane at 20° gave 1.0300, which may not be strictly correct on account of the small quantity of the material.

In determining the boiling-point of this decane, 50 cc. of the oil, purified as thoroughly as possible, distilled at 173°.6–174°.6, mostly below 174°, under a tension of 760 mm. and with the mercury column all within the vapor.

The boiling-point of normal decane was given by Krafft[1] as 173° at 760 mm., but 0.7304, its specific gravity at 20°, is sensibly lower than that of the decane from petroleum. Whether this be due to the presence of a small amount of decanaphtene, which appears to be nearly inert toward the methods of

[1] Ber. d. chem. Ges., **15**, 1695.

purification that have been applied to these petroleum hydrocarbons, can only be determined by more extended experiments. In view of the ease in chlorination of the hydrocarbons, $C_n H_{2n+2}$, and the difficulty in chlorinating the naphtenes according to the experience of Markownikoff and Oglobine, perhaps fractional chlorination should permit of the removal of decane, and the naphtene would reveal its presence by analysis. As already shown in the case of Pennsylvania dodecane, the portion remaining after incomplete chlorination is the hydrocarbon $C_{12}H_{24}$.

Hendecane, $C_{11}H_{24}$, 195°–196°.

Above 173° (760 mm.), fractions collected irregularly and in small amounts to 188°. There was no indication of an accumulation in the vicinity of 180°, but after precipitation of the sulphur compounds with mercuric chloride considerable quantities collected at 188°–192° (730 mm.), which for the most part came together at 189°–191°. An analysis of the crude distillate gave the following percentages of carbon and hydrogen:

0.1444 gram of the oil gave 0.2536 gram CO_2, and 0.1888 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.67
H	14.29	14.53

A specific-gravity determination at 20° gave 0.7789, and a determination of its vapor-density by the Hofmann method the following value:

0.1286 gram of the oil gave 67 cc. of vapor at 182°, and under 357.5 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.26

As in the corresponding crude Pennsylvania distillate, the percentage-composition of this hendecane based on the above analysis supports the formula $C_n H_{2n}$. Its specific gravity is nearly the same as that found by Warren, who gave the formula $C_n H_{2n}$; it is even closer to the value 0.7780, found by Pelouze and Cahours in their distillate from Pennsylvania, or rather from American petroleum. Pelouze and Cahours alluded

to distillates prepared from Canadian petroleum, as well as from American petroleum, and their high specific gravity, much higher than Pennsylvania distillates yield, would seem to indicate that they had in hand Canadian distillates. Another portion of the crude distillate 189°–190° was agitated with a mixture of nitric and sulphuric acids, and allowed to stand some time after the heat of the first reaction had moderated. A heavy nitro compound separated, which crystallized on standing. The reaction was far more energetic than in the same distillate from Pennsylvania petroleum, probably on account of a larger proportion of aromatic hydrocarbons. A heavy nitro compound immediately separated as an oil, which crystallized on standing. It was purified by crystallization from alcohol, in which it was very sparingly soluble, and gave as its melting-point 158°–160°, which was not changed by several crystallizations. There are several aromatic hydrocarbons whose boiling-points are in this vicinity, but only one forms a nitro derivative with this melting-point, isodurol, whose trinitro derivative melts at 156°. It would be interesting to examine these nitro products more fully, but for want of time and material, nothing further was done with them.

The specific gravity of the oil was very sensibly diminished by the action of the acid mixture. The first determination gave 0.7688, which was not diminished by further treatment, although this value is somewhat higher than the specific gravity of the Pennsylvania distillate, 0.7581. In determining the boiling-point of this product, 50 cc. distilled entirely at 195°–196°, mostly at 196°, under a tension of 760 mm. After purification of a portion of the crude distillate with fuming sulphuric acid, different preparations of the washed and dried oil gave in the hands of different analysts the following percentages of carbon and hydrogen :

I. 0.1508 gram of the oil gave 0.4683 gram CO_2, and 0.2055 gram H_2O.

II. 0.1520 gram of the oil gave 0.4715 gram CO_2, and 0.2109 gram H_2O.

III. 0.1523 gram of the oil gave 0.4733 gram CO_2, and 0.2180 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.	III
C	84.63	84.70	84.61	84.75
H	15.38	15.15	15.42	15.90

The specific gravity of the purified oil was found to be 0.7737 at 20°, and the vapor-density as follows:

0.1421 gram of the oil gave 68.6 cc. of vapor at 182°, under 373.8 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.43

A determination of its molecular weight by Mr. Hudson gave 158; required for the formula $C_{11}H_{24}$, 156.

In attempting to form the chlorine derivatives of this hydrocarbon, 16 grams of the fraction 196°, Ohio petroleum, the small amount that remained for this experiment, was treated with chlorine until it gained in weight 4.5 grams. After the chlorine product was fractioned four times it collected in very small quantity at 150°–155°. Analysis gave results corresponding to the formula $C_{11}H_{23}Cl$.

I. 0.2042 gram of the substance gave 0.1548 gram AgCl.

II. 0.1938 gram of the oil gave 0.4765 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	II.
C	69.29	....	69.64
H	12.07	....	11.88
Cl	18.63	18.71	....

Evidently the chlorination had proceeded so far that the monochlorhendecane could not be separated completely from the dichlor derivative, as shown by the high boiling-point, and the large percentage of carbon.

The small amount of the dichlor derivative was not sufficient when purified to give satisfactory analytical data in support of its composition.

Dodecane, $C_{12}H_{26}$, 214°.

Above 193° the fractional separation was continued longer *in vacuo*. At the end of the eighteenth distillation, between 120° and 130°, 1200 grams collected in single degree fractions, for the most part at 122°–124° and 128°–130°.

The latter distilled under atmospheric pressure at 212°–214°, and was therefore selected for the study of the hydrocarbon which according to the corresponding distillate in Pennsylvania oil should be $C_{12}H_{24}$. The crude distillate gave the following percentages of carbon and hydrogen :

	Calculated for $C_{12}H_{24}$.	Found.
C	85.51	85.76
H	14.49	14.55

The specific gravity of this distillate at 20° was 0.7877. 25 grams of the crude distillate was heated with fuming sulphuric acid to 50°, and kept warm on the steam-bath during several hours. Very little sulphurous acid was set free, although the acid became thick and dark. The loss in weight of the oil was 4.5 grams, or 18 per cent. The remaining oil was washed with sodic hydrate and water, and dried over sodium for analysis.

0.1500 gram of the oil gave 0.4650 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{12}H_{22}$.	Found.
C	84.70	84.54
H	15.30	15.47

A determination of its specific gravity at 20° gave 0.7867, with scarcely any change by the action of the fuming acid. Another portion of the crude distillate was shaken with a mixture of nitric and sulphuric acids. The great heat of the reaction was controlled by cooling, and the heavy nitro product allowed to separate by standing. The principal reaction was soon over, the nitro compound separating in needles on standing.

The nitro derivative was readily soluble in hot, but quite insoluble in cold, alcohol. It melted at 165°, and was doubtless a derivative of one of the aromatic hydrocarbons with boiling-points in this vicinity, such as isohexylbenzol, or isoamylbenzol, boiling-points 212°–214°, which are very probably contained in petroleum. After treatment with the acid mixture, the oil was boiled with tin and hydrochloric acid, washed, and boiled with sodium, and then distilled. Its boiling-point was not appreciably changed, but

the specific gravity was reduced to 0.7727, a value practically the same as that of the Pennsylvania decane. A determination of its molecular weight by the Beckmann method gave 172; required for $C_{13}H_{28}$, 170.

In forming the chlorine derivatives of this hydrocarbon, 35 grams absorbed 8.5 grams of chlorine, and the product was fractioned under 80 mm. After the tenth distillation about 15 cc. collected at 150°–160°. In this instance, as in one or two others, the distillate taken for chlorination was not purified, and in the distillation the vapors affected the eyes seriously, doubtless on account of substitution in the side chain in the aromatic hydrocarbons contained in the crude distillate. Either on account of decomposition, or want of sufficient material for complete separation, it was not possible to purify this product sufficiently to give satisfactory numbers on analysis, although the results show the formation of a mono- and a dichlordodecane. The amount of chlorine in the distillate 150°–160° came two per cent. too low for monochlordodecane, and no combustion was made. In a higher distillate collected at 190°–200° the following numbers were obtained:

I. 0.2224 gram of the oil gave 0.2607 gram AgCl.

II. 0.1952 gram of the oil gave 0.4411 gram CO_2, and 0.1816 gram H_2O.

	Calculated for $C_{13}H_{24}Cl_2$.	Found. I.	Found. II.
C	60.26	....	61.63
H	10.04	....	10.33
Cl	29.71	28.99	....

While, therefore, the formula of dodecane in Ohio petroleum is not supported by such reliable data as those of the lower constituents, the presence of this hydrocarbon seems to be established beyond question.

The principal constituents of Ohio petroleum have been shown to be identical with those of Pennsylvania petroleum. The higher specific gravity and peculiar qualities of the Ohio distillates depend on the larger proportions of aromatic hydrocarbons, and perhaps of other heavy constituents.

Constituents of Canadian Petroleum from Corniferous Limestone.

In continuing the study of the higher portions of Canadian

petroleum, the vacuum-distillates 150°–300°[1] were carried through fifteen additional distillations under 50 mm. As the separations proceeded, the fractions fell 50° or more in boiling-points, large portions collecting below 220°, the point where the separations could be continued without serious decomposition under atmospheric pressure. In single degree fractions after the fifth distillation was continued until the operation had been repeated in all twenty-nine times. As in the other oils, the distillates collected mainly at 159°–161°, 168°–170°, 188°–191°, and 208°–210° (730 mm.) There is even greater necessity in the Canadian than in the Ohio oil that the earlier distillations be carried on *in vacuo*, on account of the greater quantity of sulphur compounds, but more especially, as will be shown in another paper, on account of the greater proportion of unsaturated hydrocarbons and the smaller proportion of the members in question that distil between 160° and 216°. It is, therefore, otherwise impossible to obtain a large proportion of these higher constituents uncontaminated by impurities due to cracking. But the vacuum-distillates are free from the intensely disagreeable odors due to cracking, which are far more pronounced than any to be obtained from Ohio oil. Nevertheless, the natural odor of these compounds, however carefully they have been protected from decomposition before purification, is more pungent than that of those from Ohio oil. Colorless when first distilled, all these distillates become colored on standing, probably on account of polymerism of the unsaturated hydrocarbons alluded to above and of other unstable bodies resembling the terpenes, which are evidently contained in petroleum. That this is the cause of the coloration we have good evidence in the polymerization and the formation of heavier oils in these unsaturated bodies after they have been separated and allowed to stand as long as two years. Furthermore, after these unstable bodies have been removed, the purified oils remain colorless permanently. The higher specific gravity observed in the first vacuum-distillate from Canadian crude petroleum is still retained in the single degree fractions, however long the

[1] This JOURNAL, 18, 63.

fractional distillation is continued. But although these portions are heavier than the distillates from Pennsylvania and Ohio oils, they are so much lighter than the naphtenes that the latter bodies cannot be present in any considerable quantity. In general, the ready and abundant formation of nitro derivatives and sulphonic acids is sufficient evidence that the greater specific gravity is due, for the most part at least, to the aromatic constituents. It is quite probable that naphtenes are present in small amounts, and that they are accountable, as has been suggested, for the extreme difficulty in removing the last traces of the less hydrogenized constituents by fuming sulphuric acid, even after vigorous treatment several times repeated. In some instances, nitric and sulphuric acids have given nitro products that have required very long and vigorous boiling with tin and hydrochloric acid for complete reduction, or an equivalent treatment with sodium. Occasionally the reduction with tin and acid has caused the separation of a heavy red oil, insoluble in the acid, and consequently not an amine.

Decane, $C_{10}H_{22}$, 163°–164°.

The composition of the principal distillates from Canadian petroleum below 150° was found to correspond to what is required by the series C_nH_{2n+2}. Above this point the distillates were small to 158°, but between this point and 162° larger amounts collected and remained persistently at 159°–160° (730 mm.). After treatment with fuming sulphuric acid, a portion of this distillate was still further fractioned until 75 grams distilled at 163°–164° under 760 mm., and with the mercury column all in the vapor. In the crude distillate before treatment with the acid, carbon and hydrogen were determined, with no other purification than drying over sodium. No less efficient means of desiccation removes the water sufficiently for analysis. But since a reddish flocculent precipitate separates when any of these distillates stand with sodium, evidently the percentages of carbon and hydrogen in the crude distillates cannot be accurately expressed by the results of combustion. The precipitation is doubtless caused in part by sulphur compounds which are not wholly removed by alco-

holic mercuric chloride, although it is observed when the quantity of sulphur is very small.

0.1610 gram of the oil gave 0.5057 gram CO_2, and 0.1989 gram H_2O.

C	85.67
H	13.72

Before treatment with the acid, a determination of specific gravity at 20° gave 0.7785. After purification with the acid the specific gravity was diminished to 0.7572, nearly the same value as that found in the corresponding fraction of Ohio oil. The penetrating odor of the crude distillate, resembling that of the aromatic hydrocarbons, disappeared entirely after treatment with the fuming acid, and the purified oil gave only the faint characteristic odor of the petroleum hydrocarbons C_nH_{2n+2}. The acid was blackened and gave off much sulphurous acid. 30 grams gave by this treatment 23.4 grams af the purified oil with a loss of 22 per cent. It is interesting to note the higher specific gravity of the unpurified distillate 163°–164° in all these oils—Pennsylvania, Canadian, and Ohio—than that of the higher distillate, 174°. This clearly indicates a larger percentage of mesitylene and perhaps of decanaphtene. The difficulty in removing entirely the heavier body would seem to indicate a trace of the latter.

After the last distillation, the oil was again treated with the fuming acid and dried over sodium for analysis.

0.1723 gram of the oil gave 0.5358 gram CO_2, and 0.2304 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Calculated for $C_{10}H_{22}$.	Found.
C	85.71	84.51	84.82
H	14.29	15.49	14.85

The oil was again subjected to the action of the acid and analyzed.

0.1561 gram of the oil gave 0.4847 gram CO_2, and 0.2127 gram H_2O.

C	84.67
H	15.14

The slight change in the percentages of carbon and hydro-

gen evidently shows the presence of a heavy body that is but slowly affected by the acid. This impurity cannot be mesitylene, since this hydrocarbon dissolves readily in the fuming acid. Another portion of the crude distillate was next vigorously agitated with a mixture of nitric and sulphuric acids, allowing the temperature to rise spontaneously nearly to 100°. As soon as the principal action ceased the mixture cooled and an oily nitro body separated, more remaining in solution. After several crystallizations from alcohol, in which it is quite insoluble, the nitro derivative melted at 225°, near the melting-point of trinitromesitylene. The hydrocarbon oil was separated from the acid and boiled several hours with tin and hydrochloric acid, which caused the yellow color to be absorbed by the acid solution, and a small amount of a heavy oil separated, insoluble in the acid, evidently a product of the vigorous reduction. The crude distillate lost 20 per cent. in weight by this purification. The oil remaining after the reduction, when shaken with fuming sulphuric acid, washed, and dried, gave only the characteristic odor of the petroleum hydrocarbons. Upon analysis it gave the following results:

0.1455 gram of the oil gave 0.4517 gram CO_2, and 0.1980 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.67
H	15.49	15.12

While these results point clearly to the composition C_nH_{2n+2} for the principal hydrocarbon with this boiling-point, they also suggest, as has already been mentioned, a constituent of Canadian oil so inert toward reagents that it cannot be removed by ordinary means. No doubt the difficulty is increased by the great dilution of this impurity in the larger body of the decane. In its behavior toward reagents, decanapthene is suggested. Whatever may be the composition of this body, it is doubtless present in largest quantity in Canadian petroleum, a smaller amount in Ohio oil, and a still smaller proportion in Pennsylvania oil. But even in the Canadian oil the proportion is evidently very small.

The formula of the principal constituent at 163° found still further support in a determination of its molecular weight by

the method of Beckmann, in which Mr. Hudson obtained 142; the formula $C_{10}H_{22}$ requiring 142.

The purified distillate 160°–161°, Canadian petroleum, behaved toward chlorine precisely like the corresponding distillates from Ohio and Pennsylvania oils. 17 grams absorbed 4 grams chlorine, and was then fractioned *in vacuo*. About 1 cc. was obtained after five distillations at 200°-204°, atmospheric pressure, without decomposition, and it gave by analysis the composition required for $C_{10}H_{21}Cl$:

I. 0.1922 gram of the substance gave 0.1536 gram AgCl.

II. 0.1873 gram of the substance gave 0.4710 gram CO_2, and 0.2070 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	Found. II.
C	68.00	....	68.58
H	11.90	....	12.30
Cl	20.11	19.77	....

The quantity of this monochlordecane was too limited to permit of further determinations, as were also the higher portions for the separation of a dichlor derivative sufficiently pure for analysis.

Having at hand a small quantity of the distillate 162°, Berea Grit petroleum, it seemed of interest to ascertain whether it would form a chlorine derivative similar to or identical with those of the oils now under examination. 30 grams of the oil absorbed 8 grams of chlorine in forty-five minutes, and when the product was fractioned it gave a small quantity at 120°-130° with the composition required for $C_{10}H_{21}Cl$.

I. 0.1931 gram of the substance gave 0.1564 gram AgCl.

II. 0.1821 gram of the substance gave 0.4486 gram CO_2, and 0.1871 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	Found. II.
C	68.00	....	67.19
H	11.90	....	11.41
Cl	20.11	20.04	....

The formation of this chlordecane confirms the results published in a former paper[1] of this series, showing a hydrocarbon $C_{10}H_{22}$ in Berea Grit petroleum with the boiling-point 162°.

[1] This JOURNAL, 18, 1.

Decane, 173°-174°.

Above 163° (730 mm.) the absence of single bodies was indicated by the small amounts of distillates to 168°, where the single degree fractions began to increase in quantity. Between this point and 173° nearly 500 grams collected, the greater portion at 169°-171°, which could not be brought closer together without further purification. After drying over sodium, analysis of this distillate gave the following percentages of carbon and hydrogen:

0.1640 gram of the oil gave 0.5151 gram CO_2, and 0.2083 gram H_2O.

C	85.66
H	14.11

A determination of the specific gravity of this distillate at 20° gave 0.7770, a value somewhat higher than the specific gravity of the corresponding Ohio distillate. For the removal of the aromatic hydrocarbons to determine the boiling-point of the principal constituent, all the fractions 168°–173° were agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued until after a few repetitions the fractions came together at 169°–170° (730 mm.), or, under 760 mm. and with the mercury column all in the vapor, at 173°–174°. By this treatment the specific graivty was reduced 0.7614, and the percentages of carbon and hydrogen changed in a proportionate degree:

I. 0.1545 gram of the oil gave 0.4810 gram CO_2, and 0.2091 gram H_2O.

II. 0.1446 gram of the oil gave 0.4485 gram CO_2, and 0.1946 gram H_2O.

III. 0.1678 gram of the oil gave 0.5204 gram CO_2, and 0.2246 gram H_2O.

	Calculated for		Found.		
	$C_{10}H_{20}$.	$C_{10}H_{22}$.	I.	II.	III.
C	85.71	84.51	84.90	84.59	84.57
H	14.29	15.49	15.04	14.96	14.89

Although these results indicate the removal of a large portion of the aromatic hydrocarbon, and Analyses II. and III. were made with specimens on which the acid had acted several hours, it is evident that the less hydrogen-

ized body was not even then entirely removed. In further confirmation of the presence still of this constituent, one of the oils treated with the fuming acid was shaken with a mixture of nitric and sulphuric acids. The solution became warm and an oily nitro product separated above the acid. Since Markownikoff preferred purification of the Russian oil with sulphuric acid to avoid the formation of objectionable nitro products, it was inferred that this acid would remove completely the aromatic bodies. But in our experience with American oils, complete purification cannot be reached with the fuming acid alone. At first we relied on decomposition of the nitro product with sodium; but this required long digestions several times repeated, and in Canadian distillates the residual hydrocarbon which contained the nitrogen could not always be entirely removed, as was shown by analysis of a portion of crude distillate purified in this manner:

I. 0.1656 gram of the oil gave 0.5156 gram CO_2, and 0.2241 gram H_2O.

II. 0.1736 gram of the oil gave 0.5419 gram CO_2, and 0.2345 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	II.
C	84.51	84.90	85.13
H	15.49	15.04	15.01

The specific gravity of this distillate was found to be 0.7618, the same as that purified by fuming sulphuric acid. Another portion of the same crude distillate was treated with the mixture of concentrated nitric and sulphuric acids. The great heat developed was controlled by cooling, and finally the heavy nitro product collected above the acid. 25 grams of the crude distillate lost 9 grams in the formation of the nitro product, equivalent to 36 per cent. In another experiment 25 grams of the crude distillate treated with fuming sulphuric acid lost 6 grams, or 24 per cent. The oil remaining after the first experiment was again treated with the mixture of acids, which caused further separation of the nitro product. For the removal of the nitro compound, the oil was boiled during several hours with tin and hydrochloric acid. The reduction was very slow and a red oil separated, leaving the

upper layer colorless. The latter was then agitated with concentrated sulphuric acid, washed, dried, and analyzed:

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

The oily nitro derivative of the aromatic hydrocarbon deposited crystals on standing, which after recrystallization from hot alcohol, in which it was very sparingly soluble, melted at 169°. The quantity obtained was insufficient for analysis.

The specific gravity of the oil purified as described above was 0.7601, and, as shown by the vigorous means of purification employed, it cannot easily be reduced, although it is materially higher than the specific gravity of the decane 173° separated from Ohio oil, 0.7513, and of the decane from Pennsylvania oil, 0.7467. But the analyses show that the principal constituent is a hydrocarbon of the series $C_n H_{2n+2}$. The molecular weight of this hydrocarbon, determined by the Beckmann method, gave Mr. Hudson 144; required by the formula $C_{10}H_{22}$, 142.

In forming the chlorine derivative of this fraction, 35 grams was exposed to the action of chlorine until it had increased in weight 12 grams. After ten distillations *in vacuo*, 5 cc. were collected at 135°–138°, which upon analysis gave values required for $C_{10}H_{21}Cl$:

I. 0.1950 gram of the oil gave 0.4835 gram CO_2, and 0.2143 gram H_2O.

II. 0.2083 gram of the oil gave 0.1672 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	Found. II.
C	68.00	67.69	....
H	11.90	12.21	....
Cl	20.11	....	19.86

The crude distillate having been used in the preparation of the chlorine derivatives, the action on the eyes during distillation was severe, doubtless due to substitution in the side chain of the aromatic hydrocarbons contained in the unpurified oil.

In distilling the higher fractions, 5 cc. collected at 170°–180° that distilled under atmospheric pressure at 205°–210°. It was shown by analysis to have the composition required for $C_{10}H_{20}Cl_2$:

I. 0.2405 gram of the substance gave 0.3214 gram AgCl.

II. 0.2059 gram of the substance gave 0.4352 gram CO_2, and 0.1772 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	Found. II.
C	56.87	....	57.69
H	9.48	....	9.57
Cl	33.65	33.02	....

The specific gravity of this dichlordecane was found to be 1.0484. A determination of its molecular weight by the Beckmann method gave 207; the formula $C_{10}H_{20}Cl_2$ requires 211.

Hydrocarbon, $C_{11}H_{22}$.

Above 173°, the absence of a definite product was shown by the small amount of the distillates to 188°. Especial attention was given to the fractions in the vicinity of 180° with reference to the possibility of a naphtene, since the naphtene $C_{13}H_{24}$, boiling at 180°–185° was separated by Markownikoff from Russian oil, and Pelouze and Cahours found a hydrocarbon $C_n H_{2n+2}$ boiling at 180°–182°, in American (Canadian?) petroleum. But the very small amounts collected within these limits precluded the presence of either of these bodies in any appreciable quantities in Canadian petroleum. The portions distilling between 188° and 200° were gradually brought together at 189°–191°. A portion of the crude distillate was treated with fuming sulphuric acid, and still further fractioned until for the most part it came together at 196°–197° under 760 mm., and with the mercury column all in the vapor. In drying the crude distillate with sodium for analysis the usual reddish flocculent precipitate separated, which doubtless changed somewhat the composition of the oil :

0.1565 gram of the oil gave 0.4921 gram CO_2, and 0.2041 gram H_2O.

C	85.74
H	14.49

This oil gave 0.7889 as its specific gravity at 20°, and, after treatment with ordinary sulphuric acid, 0.7856, the slight difference indicating that this acid has very little action in the cold on this distillate, although the acid was considerably blackened, and sulphurous acid was observed. Another portion of the crude distillate with fuming sulphuric acid developed no heat, and when warmed on the steam-bath the acid was only slightly colored. After this treatment the specific gravity was 0.7832, nearly the same as before. A third portion of the original distillate was agitated with a mixture of concentrated nitric and sulphuric acids. Very little heat was developed, and the mixture was then warmed on the steam-bath. A small amount of nitro product separated as an oil, which crystallized on standing. After crystallization from alcohol, the nitro derivative melted at 150°–154°, near the melting-point of dinitroisodurol, 156°. After heating a long time with sodium, until there was no further action, the specific gravity was found to be 0.7785. The purified oil was submitted again to the same treatment, when its specific gravity was 0.7758. Still another treatment of the same oil with the mixture of the acids and boiling with sodium, also boiling with tin and hydrochloric acid, and agitating with fuming sulphuric acid, reduced the specific gravity only to 0.7729. Analysis I. was made of the oil after the first treatment with the mixture of acids and sodium, and Analysis II. of the oil after the third treatment :

I. 0.1562 gram of the oil gave 0.4901 gram CO_2, and 0.2051 gram H_2O.

II. 0.1628 gram of the oil gave 0.5093 gram CO_2, and 0.2095 gram H_2O.

	Calculated for		Found.	
	$C_{11}H_{24}$.	$C_{11}H_{22}$.	I.	II.
C	84.70	85.71	85.57	85.33
H	15.30	14.29	14.59	14.30

A determination of the molecular weight by the method of Beckmann gave 154; the formula $C_{11}H_{22}$ requires 154.

These results indicate the series C_nH_{2n}, and that the series C_nH_{2n+2} has ceased to represent the principal composition of Canadian petroleum at the boiling-point 196°. But

with reference to the series of hydrocarbons that are now recognized as constituting the main body of petroleum, it is not easy to classify this hydrocarbon. It is certainly not an unsaturated member of the ethylene series because it lacks additive power for the halogens, fuming sulphuric acid, etc. Its specific gravity is much less than that of the naphtene that Markownikoff and Oglobine separated at 196°–197° from the Russian oil, 0.8010 at 20°. But it is interesting to observe that the specific gravity of this hydrocarbon is practically the same as Pelouze and Cahours found in the hydrocarbon separated by them at 196°–200° from American petroleum, and which yielded them analytical values, as has already been explained, page 438, corresponding closely to the formula $C_{11}H_{24}$. Since the specific gravity of Pelouze and Cahours is so much larger than that of the crude distillate from Pennsylvania petroleum, 0.7673, it is difficult to escape the conviction that their distillates were prepared from Canadian petroleum, especially since they allude to an examination of oil from Canada, although the source of this particular oil from which were separated the individual hydrocarbons which they described is not evident from their statement.

In studying the constituents of Pennsylvania oil, it was shown that chlorine acts less readily on the principal hydrocarbons than on other constituents. Since this difference in the action of chlorine seemed to afford a means of ascertaining whether Canadian distillates contain any of the series C_nH_{2n+2}, a small quantity, 16 grams of the distillate 189°–190° purified with fuming sulphuric acid, remaining after the examination already described, was exposed to the action of chlorine until 3 grams was absorbed, and the product was fractioned *in vacuo* until a small portion, 6 grams, distilled at 189°–190°, atmospheric pressure. This fraction was boiled with sodium to remove, so far as possible, any chlorine derivative remaining, shaken with sulphuric acid, and again distilled. There was finally obtained about 3 grams that gave percentages of carbon and hydrogen agreeing fairly well for $C_{11}H_{24}$. The low values are due to a small amount for chlorine that was not entirely removed by treatment with sodium :

0.1558 gram of the oil gave 0.4803 gram CO_2, and 0.2115 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.70	84.09
H	15.30	15.09

In the formation of chlorine derivatives from the purified fraction 196°, Canadian petroleum, 25 grams absorbed 7 grams chlorine. After five distillations *in vacuo*, 3 cc. collected at 145°–150°, which distilled at 220°–228°, atmospheric pressure, and by analysis gave the values required for $C_{11}H_{21}Cl$:

I. 0 2378 gram of the substance gave 0.1747 gram AgCl.

II. 0.2005 gram of the oil gave 0.5105 gram CO_2, and 0.2097 gram H_2O.

	Calculated for $C_{11}H_{21}Cl$.	Found. I.	Found. II.
C	70.03	....	69.44
H	11.14	....	11.62
Cl	18.83	18.18	....

A determination of the specific gravity of the monochloride at 20° gave 0.8882. With the small quantity of the higher distillates, it was not possible to separate a dichlor derivative in anything like pure condition.

The small amount of the monochloride evidently precluded the possibility of ascertaining with any precision its true boiling-point, and the analysis is chiefly of value in determining the number of carbon atoms in the molecule. The number of carbon atoms received still further confirmation in a determination of the molecular weight by the Beckmann method, which gave 187; the formula $C_{11}H_{21}Cl$ requires 188.5.

Hydrocarbon, $C_{12}H_{24}$.

Above 195° (730 mm.) the distillates were small in quantity to 208°, but between 208° and 212° about 300 grams collected, for the most part at 208°–210°. The specific gravity of the crude distillate was found to be 0.7947, and analysis gave the following percentages of carbon and hydrogen:

0.1554 gram of the oil gave 0.4878 gram CO_2, and 0.1982 gram H_2O.

	Required for CnH_{2n}.	Found.
C	85.71	85.57
H	14.29	14.18

In order to collect this distillate more closely, a portion of the crude oil was treated with fuming sulphuric acid, washed, dried, and the distillation continued. 37 grams of the oil gave 27 grams after purification. After several distillations it collected at 212°–214° under 745 mm., and with the mercury all within the vapor. Two determinations of specific gravity at 20° gave (I.) 0.7851, and (II.) 0.7857. The carbon and hydrogen were also determined:

0.1586 gram of the oil gave 0.4960 gram CO_2, and 0.2105 gram H_2O.

	Calculated for $C_{19}H_{34}$.	Found. I.
C	85.71	85.27
H	14.29	14.74

These values point to the composition C_nH_{2n} for this constituent of the Canadian oil. In further evidence as to the correctness of this result, another portion of the crude distillate was shaken with a mixture of concentrated nitric and sulphuric acids, the intense heat at first generated controlled, and after the principal action had ceased the solution was kept warm for some time on the steam-bath. An oily nitro product collected above the acid in considerable quantity, but it was not further examined. The hydrocarbon remaining was then agitated with concentrated sulphuric acid, washed with caustic soda, which removed much more of the nitro product from the oil, then with water, and boiled for some time with tin and hydrochloric acid.

The oil remaining was then washed, dried, and warmed during several hours with fuming sulphuric acid, which produced little change, and boiled with sodium. After this purification, analysis still gave values required for a hydrocarbon C_nH_{2n}:

I. 0.1383 gram of the oil gave 0.4332 gram CO_2, and 0.1849 gram H_2O.

II. 0.1406 gram of the oil gave 0.1856 gram H_2O.

	Calculated for $C_{19}H_{34}$.	Found. I.	II.
C	85.71	85.41	Lost
H	14.29	14.86	14.68

In forming the chlorine derivatives of this hydrocarbon, 26.5 grams of the fraction 214°–216° was allowed to absorb chlorine until the weight had increased 9.5 grams, and the product was fractioned eight times *in vacuo*; 5 cc. collected at 160°–170°, which gave, on analysis, the percentage-composition required for $C_{12}H_{23}Cl$.

I. 0.2059 gram of the substance gave 0.1515 gram AgCl.

II. 0.2064 gram of the substance gave 0.5357 gram CO_2, and 0.2128 gram H_2O.

	Calculated for $C_{12}H_{23}Cl$.	Found. I.	II.
C	71.06	....	70.79
H	11.30	....	11.46
Cl	17.53	18.20	....

The specific gravity of this chlorine derivative determined at 20°, was found to be 0.8960. The small quantity of distillate collected within higher limits did not permit of the separation of a dichlor derivative in a pure condition. A chlorine determination gave 27.21; required for $C_{12}H_{22}Cl_2$, 29.95. It formed a thick viscous oil that could scarcely be distilled even *in vacuo* without decomposition. At a temperature slightly higher than that at which this product was collected the distillate was largely decomposed.

The series having been determined by these numbers, the number of carbon atoms was demonstrated by the molecular weight, which was found by the Beckmann method to be 172; the formula $C_{12}H_{24}$ requires 168.

What has been said as to the probability that Pelouze and Cahours worked with Canadian petroleum receives further support in comparing their results on the hydrocarbon they separated boiling at 216°–218° with those described above, although certain important differences appear between their results and mine.

The specific gravity assigned by them to the hydrocarbon 216°–218° was 0.796 at 20°, which is practically the same as the specific gravity of my crude distillate, 0.7947, given above. But their description of the properties of this distillate are not in accordance with my observations. Referring to the action of reagents on their product, they state: "Le brome, l'acide

azotique fumant, l'acide sulfurique fumant, ainsi que le mélange de ces deux acides se comportent à son égard comme avec le composé précédent." And after stating, in the description of the preceding compound, that it is not attacked in the cold by bromine, fuming nitric acid, sulphuric acid at the maximum of concentration with nitric acid, nor by fuming sulphuric acid, they state: "Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition." That this observation does not represent correctly the behavior of this distillate from Pennsylvania, nor Ohio, nor Canadian petroleum, has been clearly shown by experiments described in this paper. It is especially inapplicable to the Canadian distillate, since this oil with a mixture of ordinary concentrated nitric and sulphuric acids, on shaking, immediately develops sufficient heat to raise the temperature to vigorous ebullition of the acid mixture, and to destroy a large portion of the hydrocarbon. In all these experiments the initial reaction had to be controlled by cooling.

Concerning the number of carbon atoms in the hydrocarbon I have separated at this point, it seems to be well established by the molecular weight, $C_{12}H_{24}$, and by the composition of the monochlor derivative, $C_{12}H_{23}Cl$. Yet in a product with a specific gravity much higher than this purified hydrocarbon, Pelouze and Cahours obtained numbers by analysis, as shown above, corresponding closely to the formula $C_{13}H_{26}$, and from the hydrocarbon a chlorine derivative, $C_{13}H_{25}Cl$, also supported by analytical values closely corresponding to the theoretical composition required for this formula.

Summary of Results.

1. That part of Pennsylvania petroleum which boils between 150° and 220° consists chiefly of decane, boiling-point 163°–164°; decane, boiling-point 173°–174°, probably normal decane; hendecane, boiling-point 196°–197°; and dodecane, boiling-point 214°–216°. It contains also in smaller proportions the series of aromatic hydrocarbons boiling within these limits. Allusion has already been made to mesitylene, cumol, pseudocumol, cymol, isocymol, durol, isodurol, and no doubt

others could be identified with sufficient quantities of the petroleum distillates.

2. The composition of Ohio Trenton limestone petroleum within the same limits is represented by the same members of the series C_nH_{2n+2}, and the higher specific gravity of these distillates is caused by a larger proportion of aromatic hydrocarbons.

3. The constituents of Canadian corniferous limestone petroleum from Petrolia, within these limits of temperature, are the same at 163° and 173°. But the hydrocarbons collecting at 196° and 214° have the composition represented by the general formula C_nH_{2n}. Probably a better knowledge of these higher distillates will be gained when the true composition of American petroleum above 220° has been ascertained. The proportion of aromatic hydrocarbons is greater in Canadian than in Ohio petroleum. There are indications in all these petroleums that the heavier constituents include other bodies than the aromatic hydrocarbons, which will require for their identification the manipulation of large quantities of distillates.

General Conclusions.

The results described in this paper make it clear that no conclusions can be arrived at concerning the composition of the principal constituents of American petroleum between 151° and 216° without separating from these bodies the various impurities with which they are contaminated in the crude distillates. However far fractional distillation may be carried, it is impossible to effect a separation of those bodies whose boiling-points do not differ by more than a few degrees. But, fortunately, the principal constituents of petroleum are not affected by reagents under conditions which allow the removal of the contaminating bodies. While the statement of Pelouze and Cahours that the portions of American petroleum under consideration are not affected by nitric acid nor by fuming sulphuric acid, is not supported by the behavior of distillates used by me in this examination, it is true that the principal constituents are not acted upon by those reagents under conditions that permit of purification. A casual ex-

amination of the literature of Pennsylvania petroleum is sufficient to reveal the uncertainty and confusion in statements concerning the composition of the portions with higher boiling-points. The principal constituents have more commonly been referred to the series C_nH_{2n+2}, as suggested by Pelouze and Cahours, who included in this series all the petroleum hydrocarbons, even the least volatile oils and paraffin, although on the basis of Warren's investigations allusions have been made to the unsaturated olefine hydrocarbons C_nH_{2n} as constituting the main body of Pennsylvania petroleum above 150°, and the belief has been expressed that the naphtene series C_nH_{2n} would best explain Warren's results. As already stated, above 150° Pelouze and Cahours separated distillates at 162°, 182°, 196°–200°, and 216°–218°, which, with no special purification, gave analytical data corresponding closely to the theoretical values for the series C_nH_{2n+2}. That there are marked differences in the specific gravity of crude and refined distillates appears in the purification of all distillates described in this paper, and it is no easy task to purify the crude distillates so that they shall yield satisfactory analytical data. As shown in the following table, the specific-gravity determinations by Pelouze and Cahours in the products they analyzed are essentially different from those in Pennsylvania distillates herein presented. The percentages of carbon and hydrogen required for the series C_nH_{2n+2} were obtained in fractions whose specific gravity was even higher than that of our crude distillates, which gave values closely agreeing with the series C_nH_{2n}. This difference in specific gravity can only be explained by assuming, which is evidently true, that Pelouze and Cahours overlooked the aromatic hydrocarbons. It does not appear in their reference to American petroleum whether they really operated on distillates from Pennsylvania oil; but on the other hand, their specific-gravity determinations are not widely different from those of distillates from Canadian oil to which occasional reference is made in their publications.

Pennsylvania Petroleum.

Fraction. Unpurified. C. F. M.	Fraction. Purified. P. & C.	Specific gravity. C. F. M.	Specific gravity. P. & C.	Series.
163°-164°		0.7684 (20°)		C_nH_{2n}
	163°-164°	0.7479 (20°)		C_nH_{2n+2}
	162°		0.757 (15°)	C_nH_{2n+2}
196°-197°		0.7673 (20°)		C_nH_{2n}
	196°-197°	0.7581 (20°)		C_nH_{2n+2}
	196°-200°		0.7780	C_nH_{2n+2}
214°-216°		0.7745 (20°)		C_nH_{2n}
	214°-216°	0.7684 (20°)		C_nH_{2n+2}
	216°-218°		0.776	C_nH_{2n+2}

Canadian Petroleum.

Fraction unpurified.	Fraction purified.	C. F. M.
163°-164°		0.7785
	163°-164°	0.7582
196°-197°		0.7889
	196°-197°	0.7729
214°-216°		0.7947
	214°-216°	0.7851

If the results of Pelouze and Cahours were readily obtained with distillates from Canadian petroleum, as seems probable, especially since Pennsylvania distillates do not yield such high values, the specific-gravity determinations in the lower distillates agree fairly well with mine in the purified Canadian hydrocarbons.

The results of Warren, on the other hand, are consistent in giving numbers that account both in specific gravity and in percentage-composition for the complex mixture that crude petroleum distillates are known to be. While Warren made no attempt to purify his distillates, they were obtained in a course of fractional separations far exceeding in efficiency those of other experimenters. It is interesting to observe in the following table how clearly the distillates from Pennsylvania petroleum analyzed by Warren resemble in specific gravity the unpurified distillates described in this paper.

Fraction unpurified.	Fraction purified.	Specific gravity. Mabery.	Warren.	Series.
163°-163°		0.7674 (20°)		$C_n H_{2n}$
173°.5		0.7502 (20°)		$C_n H_{2n}$
	173°.5	0.7445 (20°)		$C_n H_{2n+2}$
175°			0.7598 (15°)	$C_n H_{2n}$
196°		0.7673 (20°)		$C_n H_{2n}$
	196°	0.7581 (20°)		$C_n H_{2n+2}$
196°-197°			0.7721 (15°)	$C_n H_{2n}$
216°		0.7745 (20°)		$C_n H_{2n}$
	216°	0.7684 (20°)		$C_n H_{2n+2}$
214°-216°			0.7804 (15°)	$C_n H_{2n}$

Warren found no single body at 162°, his other hydrocarbons correspond in boiling-points with those described in this paper. The series $C_n H_{2n}$ of Warren, with a series of the same numerical composition in Russian oil, led to the suggestion that the naphtenes might form an essential part of Pennsylvania oil. This belief was encouraged by statements that found their way into works on petroleum, that Markownikoff discovered the naphtenes also in Pennsylvania oil. The statement that Markownikoff investigated Pennsylvania petroleum is indeed erroneous,[1] and a closer study shows that the naphtenes cannot be contained in Pennsylvania petroleum in any considerable quantity on account of their higher specific gravity as already shown :

Fraction. unpurified.	Fraction purified.	Specific gravity. Mabery.	Markownikoff.	Series.
163°-164°		0.7684		$C_n H_{2n}$
	163°-164°	0.7479		$C_n H_{2n+2}$
	160°-162°		0.795 (0°)	$C_n H_{2n}$
	180°-185°		0.8119 (0°)	$C_n H_{2n}$
196°-197°		0.7673		$C_n H_{2n}$
	196°-197°	0.7581		$C_n H_{2n+2}$
	196°		0.8055 (14°)	$C_n H_{2n}$
214°-216°		0.7745		$C_n H_{2n}$
	214°-216°	0.7684		$C_n H_{2n+n}$

Even the mixtures that the crude Pennsylvania distillates have proved to be have a much lower specific gravity than those with the same boiling-points from Russian oil. After purification, the Pennsylvania distillates unquestionably have the composition of the series $C_n H_{2n+2}$.

[1] In a private communication, I am informed by Professor Markownikoff that he has not included Pennsylvania petroleum in his investigations.

Allusion has been made to the great difficulty in removing entirely the constituent with less hydrogen from the distillates prepared for analysis, and also to the fact that, even after the most thorough purification, the specific gravity of the purified distillate is appreciably higher than that of the hydrocarbon with the same boiling-point prepared by synthetic methods. These facts may indicate the presence in small quantity of naphtenes which are acted on only very slowly by reagents, especially when largely diluted in the main body of the principal constituent.

Structure of the Petroleum Hydrocarbons, 160°–216°.

In comparing the petroleum hydrocarbons with the corresponding bodies synthetically prepared, it is but fair to state that the literature of the latter is not altogether satisfactory. The properties of normal decane as it was prepared by Lachowicz,[1] by the action of sodium on a mixture of normal octyl bromide and ethyl iodide, and also by Krafft,[2] by heating caprinic acid with a mixture of hydriodic acid and phosphoric pentachloride, seem to define the corresponding petroleum hydrocarbon as the normal compound.

The boiling-point of the hydrocarbon synthetically prepared is 173° under 760 mm., and the specific gravity 0.7456 at 0°. The boiling-point assigned by me to petroleum decane is 173°.5, and its specific gravity at 20° is (from Pennsylvania petroleum) 0.7486. Evidently the decane obtained by Thorpe and Young by heating solid paraffin, boiling at 166°–168°, specific gravity 0.7394 at 13°.5, is an impure normal hydrocarbon.

A decane has been obtained by several methods, boiling at various temperatures between 157° and 162°. Active diamyl boiling at 159°–162°, specific gravity 0.7463 at 22°, with a high dextro rotatory power, was obtained by Just, on treating active amyl iodide with sodium. But the petroleum decane has not the same form, since it shows no influence on polarized light. The latter has with greater probability the same form as diisoamyl, obtained by Würtz on heating isoamyl iodide with sodium. The boiling-point of this secondary decane is given

[1] Ann. Chem. (Liebig), **220**, 179. [2] Ber. d. chem. Ges., **15**, 1695.

by Würtz as 158°, with no mention of barometric tension, and its specific gravity as 0.7413. Petroleum decane boils at 163°, and its specific gravity at 20° is 0.7479. In a similar reaction using amyl bromide, Grimshaw[1] obtained a decane boiling at 168°, under 751 mm. Either the normal bromide must have been used in this reaction giving normal decane, or the boiling-point of the product is too high.

Normal hendecane (or undecane) was prepared by Krafft[2] from the aldehyde rautenol by the same reaction that he used for decane. Its boiling-point is given as 194°.5 under 760 mm., and the specific gravity as 0.7411 at 20°. Since the boiling-point, 196°–197°, and specific gravity, 0.7581, of petroleum hendecane and the formula of this body, $C_{11}H_{24}$, determined by its molecular weight, corresponded so closely to normal hendecane, it has doubtless the same form. As already explained, the higher specific gravity may be due to a small proportion of a naphtene.

The formula $C_{12}H_{26}$, which represents the petroleum hydrocarbon boiling at 214°–216°, is supported by that of normal dodecane which Krafft[3] obtained by the reduction of laurinic acid. Normal dodecane boils at 214°.5, atmospheric pressure, and its specific gravity at 20° is 0.7511. The specific gravity of petroleum dodecane was found to be 0.7729.

Relation between Specific Gravity and Chemical Composition of Petroleum Distillates.

One interesting result of the examinations described in this paper, and other papers of this series, is the relation between the chemical composition of the individual hydrocarbons and the density of the crude oils from which they were prepared. Pennsylvania petroleum with the lowest specific gravity, 0.80–0.82, is composed below 220° of the hydrocarbons $C_n H_{2n+2}$. Ohio oil, next higher in the scale of specific gravity, 0.82–0.85, still contains below 220°, as its principal constituents, hydrocarbons of the same series. As the density increases in the Canadian oil, specific gravity 0.85–0.88, the series $C_n H_{2n+2}$ represents the principal constituents up to and in-

[1] Ber. d. chem. Ges., **10**, 1602. [2] *Ibid.*, **10**, 1697.

[3] *Loc. cit.*, 1698.

cluding decane, boiling-point 173°, the higher members having the composition C_nH_{2n}. Both oils with higher specific gravity, such as South American petroleum, specific gravity 0.9480, described in another paper of this series, contain only hydrocarbons of the series C_nH_{2n}, and in Caucasus petroleum, specific gravity 0.88, Markownikoff and Oglobine found as the principal constituents the naphtenes, series C_nH_{2n}.

Action of Sulphuric Acid on Petroleum Distillates.

Since the beginning of the petroleum industry, the sole method of refining has depended on agitation with sulphuric acid; yet, notwithstanding the large quantities of material that sulphuric acid removes, as shown by the immense sludge heaps in the vicinity of the refineries, the refiner has not the slightest notion as to what the acid accomplishes beyond his principal object, which is to prepare acceptable products for the market. Neither has any scientific study been made of this problem, at least in American petroleum, so far as revealed by published statements; but that this is an interesting as well as a difficult subject appears from results described in several papers of this series. That ordinary concentrated sulphuric acid has some effect on the density of petroleum distillates is evident from numerous experiments described in this paper. But without independent evidence, it cannot be determined just what constituents are affected by the acid. That some of these constituents, present in small quantity, are unstable and easily acted on by reagents is evident. The refiner must avoid an elevation of temperature during treatment with the acid, otherwise a color appears in the oil that is difficult to remove without redistillation. Evidently an increase in temperature permits of troublesome chemical changes between the acid and the oil, with the formation of products that remain in solution. The skillful refiner is also careful to remove the acid by washing before adding caustic soda to avoid an objectionable color.

In studying the action of sulphuric acid on different distillates from the Russian oil, Markonikoff and Oglobine[1] attributed the influence of the acid mainly to its action on the un-

[1] Ann. chim. phys. (6), **2**, 404.

saturated hydrocarbons and the oxygen compounds. Having separated a series of unsaturated hydrocarbons from Canadian petroleum (Mabery and Quayle, unpublished results), and having ascertained the presence of the same bodies in Ohio petroleum,[2] on account of their unstable character and the ease with which they polymerize alone, or more readily when in combination with sulphuric acid, we are convinced that one important office of the acid is the removal of these compounds. With reference to the oxygen compounds in American petroleum, they seem to collect, for the most part at least, in the distillates above 225°. In the composition of their unpurified distillates Markonikoff and Oglobine found a considerable difference between the total percentages of carbon and hydrogen and 100 per cent., which they assigned to oxygen. In analysis of unpurified distillates described in this paper, the total percentages of carbon and hydrogen in most instances have approached 100 per cent. to within the limit of the error of analysis, although it is true that these distillates were subjected to close fractional distillation within 1°, while those of Markownikoff and Oglobine were distilled only a few times within limits of 5°. In all the distillations of Pennsylvania, Ohio, and Canadian petroleum, a slight coloration of the still-residue after a long series has been observed, which may be caused by a small amount of oxygen compounds.

On standing with metallic sodium, all the unpurified distillates described in this paper deposit flocculent precipitates, more or less colored, which are evidently products of decomposition. This cannot be due to the action on the principal hydrocarbon, since, when purified, such action by sodium is not observed. Neither should the aromatic hydrocarbons behave in this manner toward sodium. These precipitates must be formed from the oxygen or the nitrogen compounds in the oils, probably from the former. They cannot be due to decomposition of sulphur compounds, since Pennsylvania oil contains only a very small percentage of sulphur, and the other distillates were all treated with alcoholic mercuric chloride. It is quite probable that ordinary sulphuric acid combines to a certain extent with some of the aromatic hydrocar-

[2] This JOURNAL., 13, 5.

bons. A more extended study of the action of sulphuric acid on a larger scale as in refining, would doubtless be interesting and profitable.

Concerning the action of fuming sulphuric acid, no further explanation is necessary than has been given in connection with the experiments which describe its behavior toward these petroleum distillates.

So far as possible, all details of this work have been carried on under my immediate and constant personal supervision. For efficient aid I am indebted to the following gentlemen: Messrs. C. A. Soch, private assistant, 1894–95; E. Davidson, 1895-96; E. J. Hudson, molecular-weight determinations, and other aid mainly in connection with the chlorine derivatives of the hydrocarbons; W. F. Priebe, who selected a portion of the work on the Pennsylvania distillates as the subject of a thesis for the degree of Bachelor of Science; and Messrs. Giessen, Watson, Worstall, Piwonka, Shaw, and Walker, for faithful assistance in the routine work of distillation and combustions.

The work now in progress includes a study of the pentanes, hexanes, and heptanes in Pennsylvania petroleum, and the composition of the portions of Pennsylvania, Ohio, Canadian, Berea Grit, and South American petroleum between 216° and 350°.

XXVII.—REFRACTIVE POWER OF THE HYDROCARBONS AND CHLORINE DERIVATIVES DESCRIBED IN THE PRECEDING PAPER.[1]

By Charles F. Mabery and Edward J. Hudson.

Within recent years the refractive power of the hydrocarbons and their derivatives has received considerable attention from Brühl, Thomsen, and others, and attempts have been made to draw conclusions based on the relation between the index of refraction and density, to define structural relations. The experimental data have been obtained for the most part from bodies with a limited number of carbon atoms, in which the differences in refractive power are large. Inde-

[1] Presented to the American Academy of Arts and Sciences, October, 1896.

pendently of determinations bearing on theoretical considerations, the refractive power of oils and solutions has been accepted on practical grounds as a valuable property for recognition and for determining degrees of purity.

While it was not to be expected that the determination of refractive power in hydrocarbons with such a large number of carbon atoms as those contained in the higher portions of petroleum would be serviceable in ascertaining the structure of individual hydrocarbons, the wide differences in specific gravity between unpurified and purified distillates led us to believe that similar differences would be observed in refractive power. When subjected to experimental proof, these differences were easily verified.

The determinations of the angle of refraction were made in the latest form of Pulfrich refractometer, made by Carl Zeiss, Jena, and the calculations of the index of refraction by the formula $I = \sqrt{N^2 - \sin^2 I}$, in which I represents the index of refraction, N the angle of the prism, and I the observed angle. The observations in this refractometer are rapidly made, and the calculations are much simplified by the use of a table arranged by Pulfrich[1] so that from the observed angle the index may read directly from the table.

In the following table giving the refractive power (the excess of the index of refraction over unity), after the numbers representing the refractive power of the distillates purified by a mixture of nitric and sulphuric acids, and with fuming sulphuric acid, the differences between the refractive power before purification and afterwards are given :

	Pennsylvania.		Ohio.		Canadian.	
			163°.0			
	Ref. power.	Dif.	Ref. power.	Dif.	Ref. power.	Dif.
Unpurified distillate	0.4241		0.4248		0.4276	
After treatment with						
HNO_3 and H_2SO_4 .	0.4083	0.0158	0.4123	0.0125	0.4133	0.0143
After treatment with						
$H_2S_2O_7$	0.4146	0.0095	0.4113	0.0135	0.4127	0.0139
			173°.5			
Unpurified distillate	0.4163		0.4239		0.4245	

[1] Zeit. für Instrumentenkunde, 1888, p. 47.

	Ref. power.	Dif.	Ref. power.	Dif.	Ref. power.	Dif.
After treatment with						
HNO_3 and H_2SO_4 ·	0.4118	0.0045	0.4134	0.0105	0.4149	0.0096
After treatment with						
$H_2S_2O_7$	0.4093	0.0070	0.4118	0.0121	0.4138	0.0107
			196°.0			
Unpurified distillate	0.4214		0.4251		0.4309	
After treatment with						
HNO_3 and H_2SO_4 ..	0.4158	0.0056	0.4214	0.0037	0.4219	0.0090
After treatment with						
$H_2S_2O_7$	0.4163	0.0051	0.4209	0.0042	0.4231	0.0078
			216°.0			
Unpurified distillate	0.4249		0.4280		0.4289	
After treatment with						
HNO_3 and H_2SO_4 ..	0.4209	0.0040	0.4244	0.0036	0.4219	0.0070
After treatment with						
$H_2S_2O_7$	0.4209	0.0040	0.4241	0.0039	0.4212	0.0077

Inspection of the columns in this table headed Refractive Power shows a gradual increase with the rise in boiling-points, less regular in the unpurified distillates, but more uniform after purification. A comparison of refractive power in the same distillates from all the oils reveals higher values in the Ohio and Canadian distillates than in those from Pennsylvania oil, analogous to the differences in specific gravity referred to in the preceding paper. In the unpurified distillate 163° from all sources, the influence of the large proportions of mesitylene is apparent.

In determining the refractive power of the monochlor and dichlor derivatives of the hydrocarbons between 160° and 216° portions of the product were used whose composition was determined by analysis, as shown in the preceding paper. On account of the limited quantities, purification was not carried as far as would have been desirable, although the proportion of other bodies was probably not sufficient seriously to affect the results. The differences in refractive power between the hydrocarbons and the monochlor derivatives, as well as those between the monochlor and dichlor derivatives are sufficient to demonstrate the influence of the chlorine atoms.

Monochlor derivatives. Distillate.			Pennsylvania.	Ohio.	Canadian.
125–130	($C_{10}H_{21}Cl$)	from 164°	0.4424		
"	"	" "		0.4470	
130–140	($C_{10}H_{21}Cl$)	" 174°	0.4445		
"	"	" "		0.4437	
146–150	($C_{11}H_{23}Cl$)	" 196°	0.4433		
"	"	" "		0.4457	
"	($C_{11}H_{21}Cl$)	" "			0.4461
140–145	($C_{12}H_{25}Cl$)	" 216°	0.4456		
"	($C_{12}H_{23}Cl$)	" "			0.4521
Dichlor derivatives. Distillate.					
160–170	($C_{10}H_{20}Cl_2$)	from 164°	0.4639		
"	"	" "		0.4770	
170–180	($C_{10}H_{20}Cl_2$)	" 174°	0.4604		
"	"	" "		0.4640	
"	"	" "			0.4676
190–200	($C_{12}H_{24}Cl_2$)	" 216°		0.4650	
"	($C_{12}H_{22}Cl_2$)	" "			0.4747

It seems peculiar that the hydrocarbon boiling at 216° obtained from Canadian petroleum, which gives analytical values corresponding to the formula $C_{12}H_{24}$, should have the same boiling-point as the corresponding constituent of Pennsylvania and Ohio oils, and that it should give a chlorine derivative with substantially the same boiling-point. Probably a better understanding of this hydrocarbon will be gained by the study of the higher constituents, which is now in progress.

Contributions from the Sheffield Laboratory of Yale University.

LII.—ON THE MOLECULAR REARRANGEMENT OF THE OXIMES BY MEANS OF CERTAIN METALLIC SALTS.

By William J. Comstock.

The conversion of ordinary benzaldoxime into its stereoisomer was discovered by Beckmann, who effected it first[1] by the action of sulphuric acid, afterwards[2] by the action of hydrochloric acid gas on the ethereal solution. This latter method has since been applied with success to other cases.

The Beckmann rearrangement of an oxime into amide or substituted amide, is effected by means of phosphorus penta-

[1] Ber. d. chem. Ges., **20**, 2766. [2] *Ibid*, **22**, 433.

chloride,[1] strong sulphuric acid,[2] acetyl chloride[3] and the so-called Beckmann mixture.[4] I have found that several metallic salts are capable of producing the same results. A good example of this is furnished by the behavior of cuprous chloride towards benzantialdoxime. When a cold solution of ordinary benzaldoxime in dry benzene or toluene is treated with cuprous chloride, the chloride dissolves rapidly. If the solution is a concentrated one, the formation of long needles can be noticed at once; if the solution is dilute, the same compound can be precipitated by the addition of petroleum ether. The new compound is an addition-product of two molecules of oxime to one of cuprous chloride, reckoned as CuCl. But instead of being an addition-product of the antioxime, it contains the stereoisomer.

If the benzene or toluene solution is shaken for a few minutes with an excess of cuprous chloride, and the filtered solution heated, a separation of cuprous chloride begins at once. After continued boiling and concentrating the filtered solution, benzamide separates. I have tested the behavior of several oximes, and found in each case that addition-products with cuprous chloride or cuprous bromide could be obtained. This is true of both aldoximes and ketoximes, and in each case the composition of the product was

$$(\text{Oxime})_2 + \text{CuCl or CuBr}.$$

The rearrangement into amide or substituted amide by boiling a solution of the cuprous-halide-oxime, is not, however, a general reaction, and where effected is not necessarily a smooth one. When the solution of cuprous-halide-oxime is heated, there is usually, if not always, to some extent a regeneration of aldehyde or ketone. In some cases the greater part of the oxime is decomposed in this latter way. For instance, on boiling a toluene solution of benzophenoneoxime with cuprous bromide, the greater part was found to be converted into benzophenone.

The tendency of an oxime to form a "molecular compound" with cuprous chloride is so great, that in two cases at least,

[1] Beckmann, *Ibid*, **19**, 988.
[2] Beckmann, *Ibid*, **20**, 1507.
[3] Victor Meyer and Warrington, *Ibid*, **20**, 500.
[4] *Ibid*, **20**, 2581.

cupric chloride is reduced to *cuprous* chloride. Benzaldoxime and acetoxime are the two compounds whose behavior towards cupric chloride has been studied.

If an aqueous solution of cupric chloride is added to a concentrated aqueous solution of acetoxime, the separation of colorless crystals begins at once, even at low temperature. With very dilute solutions the separation is slower, but the same reaction takes place. These crystals are identical in composition with those formed by the direct action of cuprous chloride on acetoxime dissolved in an anhydrous solvent. As soon as the separation of crystals from the aqueous solution of oxime and cupric chloride begins, the solution shows the presence of nitrous acid by its reaction with potassium iodide solution.

Obviously a portion of the oxime is split into acetone and hydroxylamine, which latter reduces the cupric chloride to cuprous chloride with formation of nitrous acid, while another portion of oxime unites with the cuprous chloride to form the difficultly soluble cuprous-chloride-oxime.

In addition to cuprous chloride and cuprous bromide, antimony trichloride effects the Beckmann rearrangement with the greatest ease. This I have shown in the case of benzophenoneoxime.

As a method of converting an antialdoxime into its stereoisomer, the action of hydrochloric acid on the ethereal solution is obviously simpler than the action of cuprous chloride or cuprous bromide. Nevertheless these changes of the oximes under the influence of metallic salts are not without interest. Whether the action of a metallic salt can lead to the discovery of a missing stereoisomeric oxime when other methods fail, is of course uncertain. No special efforts have been made with this in view, as the group has already been worked up with considerable thoroughness.

In compounds other than oximes, but containing the group —N=C—, the methods of obtaining the two stereoisomeric forms are by no means as satisfactory ; and there is no *a priori* reason why, in some of these other cases, a rearrangement should not be effected by the action of metallic salts.

Cuprous chloride, cuprous bromide, and antimony trichlo-

ride, all add, with the greatest ease to some of Schiff's bases. A few of these derivatives I shall describe in another paper.

Experimental Part.

Cuprous-chloride-benzsynaldoxime, $(C_6H_5CH=NOH)_2CuCl$. —The best method of preparing this compound is by treating a cold solution of ordinary benzaldoxime in dry toluene with a slight excess of cuprous chloride, shaking gently until no more chloride dissolves. From the filtered solution the cuprous-chloride-oxime can be precipitated by the addition of petroleum ether. The toluene solution can even be warmed gently. On working with weighed quantities it was found that the solution of ordinary benzaldoxime dissolved a little less cuprous chloride than is represented by the above composition. The compound crystallizes in needles which are at first practically colorless, although the solution assumes at once a yellowish-brown color. The crystals become dark on standing in contact with the mother-liquor, and become dark green very quickly when exposed to the air.

The compound has no sharp melting-point. Washed with petroleum ether and dried *in vacuo* it was found to contain 19.1 per cent. of copper. The above composition requires 18.59 per cent. of copper.

By treatment with cold dilute sodium hydroxide solution the copper can be removed and on leading carbonic acid into the filtered solution, benzsynaldoxime separates at once in crystals.

From cupric chloride the compound was obtained as follows: The ordinary oxime was dissolved in alcohol and mixed with an alcoholic solution of cupric chloride; water was then added until the solution became turbid, a drop of hydrochloric acid added, and the mixture kept at ordinary room temperature. The formation of long colorless needles began within a few minutes, but the separation was not complete for several hours. The compound prepared in this way seemed comparatively stable when in contact with the mother-liquor, but showed the same rapid coloration when exposed to the air.

When washed quickly with a small quantity of 50 per cent.

alcohol, and dried *in vacuo*, it gave the following analytical results :

	Found.	Calculated.
Cu	18.8	18.59
Cl	11.7	10.40

Benzsynaldoxime was obtained from this product in the manner described above. The same compound can be obtained by adding ordinary benzaldoxime to a cold solution of cuprous chloride in dilute hydrochloric acid. When the oxime is added to a cold concentrated solution of cuprous chloride in strong hydrochloric acid, a compound crystallizing in small yellow needles is formed. This yellow compound is quite unstable, but it contains the oxime as syn-oxime (shown as above), and is obviously a double salt, as it is formed only in presence of strong acid. On adding water gradually to this double salt, the formation of the white needles of cuprous-chloride-oxime can be observed.

As to the rearrangement into benzamide, it was carried out in benzene and in toluene solution. The amide was obtained with sharp melting-point after one recrystallization, and was further identified by the formation of ammonia and benzoic acid. The cuprous chloride which separated when this rearrangement was effected, was dirty and mixed with some resinous matter after the solution had been heated for a time, although when the separation first began it was light colored, much lighter than the solution. Benzaldehyde and probably benzonitrile are by-products of the reaction.

I have assumed that the copper separates as cuprous chloride or cuprous bromide in this and similar cases, but have not proved this by analysis.

Cuprous bromide acts like the chloride, but I have not analyzed the intermediate product, which, however, seemed more stable than the cuprous chloride compound.

Other Aldoximes.—Cinnamaldoxime gives with cuprous bromide an addition-product crystallizing from toluene in small yellow needles. For this purpose a mixture of the two stereoisomers[1] was used.

Found Cu = 14.52 ; calculated for $(oxime)_2CuBr$, Cu = 14.49.

[1] See Bamberger and Goldschmidt : Ber. d. chem. Ges., **27**, 3428.

It was shown that the Beckmann rearrangement is effected by boiling the toluene solution. The amide of cinnamic acid was not purified, but decomposed by boiling sodium hydroxide solution. Pure cinnamic acid was obtained and identified. Much aldehyde was also formed.

Oenanthaldoxime forms a beautifully crystallized product with cuprous bromide when warmed in ligroïn solution. On cooling the filtered solution the product separates in star-like clusters of long transparent prisms. It proved comparatively stable when exposed to the air; after several hours there was practically no change. The amount of oenanthol regenerated when the toluene solution was boiled seemed large.

Cuprous-chloride-acetoxime, $(C_2H_4NOH)_2CuCl$.—This compound can be prepared in dry benzene, toluene, or ligroïn by the direct action of cuprous chloride. It can be recrystallized advantageously from boiling ligroïn, but undergoes some decomposition on protracted boiling, and changes very quickly on exposure to the air. It crystallizes in colorless transparent plates or inclined prisms, which assume a yellowish color on exposure to the air for a few minutes. The melting-point is not sharp; it softens below 80°, and is completely melted at 96° to a clear fluid of yellowish brown color. On further heating it undergoes energetic decomposition, and has an odor like impure acetamide. The change is, however, essentially a dissociation.

An analysis of the compound crystallized from hot ligroïn gave the following results:

	Found.	Calculated.
Cu	26.17	25.88
Cl	14.61	14.49

The preparation from cupric chloride in aqueous solution has been described in the introduction. An analysis of the compound prepared in this way and dried *in vacuo* without recrystallization gave the following results:

	Found.	Calculated.
Cu	26.70	25.88
Cl	14.83	14.49

On recrystallization from ligroïn the crystals were to the

eye exactly like those prepared directly from cuprous chloride.

Cuprous-bromide-acetoxime, $(C_2H_4NOH)_2CuBr$. — Preparation as in the case of the previous compound. The bromide is changed less rapidly on exposure to the air and is more difficultly soluble. It melts to a clear fluid at 121°–122°, after softening a few degrees below. It occurs as hexagonal plates or thick, transparent, inclined prisms. A copper estimation gave 22.05 per cent., while the theory requires 21.90 per. cent.

The Beckmann rearrangement into methylacetamide could not be effected by boiling the toluene solution of either of these acetoxime derivatives. A solution of the cuprous-bromide-oxime was boiled for hours. The solution became dark colored, and a small quantity of insoluble matter was formed. After boiling off most of the toluene, the entire residue was boiled with strong sodium hydroxide solution, the volatile part being caught in dilute hydrochloric acid. The hydrochloric acid solution left a residue on evaporation, but this residue was not methylamine hydrochloride, as it was not deliquescent and did not give the isonitrile reaction. The distillate from the sodium hydroxide had a distinct bone-oil odor and this same odor was noticed on adding an alkali to the residue from the hydrochloric acid solution. This suggests the formation of a pyridine base, but I did not obtain sufficient for identification.

Other Ketoximes.—Acetophenoneoxime in toluene solution unites with cuprous chloride. The compound was precipitated by ligroïn in thin colorless plates, which darken quickly. Unchanged oxime was recovered after treating with sodium hydroxide solution, filtering and adding carbon dioxide.

Found Cu = 17.7 ; calculated Cu = 17.2.

Boiling in toluene solution led to dark-colored products not carefully examined. Certainly the reaction is not a smooth one.

Benzophenoneoxime and Cuprous Chloride, $\left(\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!C\!=\!NOH\right)_2$ CuCl.—This compound was prepared as follows : The oxime was dissolved in methyl alcohol, an excess of cuprous chlo-

ride and a few drops of hydrochloric acid added, the solution warmed on the water-bath to 60° for a few minutes, and filtered from the excess of chloride. On cooling small, thick, yellow plates were deposited. Unchanged oxime could be recovered.

Found, 14.08 per cent.; calculated, 12.86 per cent. copper.

The compound can be obtained in large diamond-shaped, doubly-terminated plates of yellow color, when an excess of cuprous chloride is dissolved, together with the oxime in a mixture of hydrochloric acid, methyl alcohol and chloroform, and the solution evaporated quickly at ordinary temperature. A toluene solution of the oxime boiled in presence of cuprous chloride or cuprous bromide, yielded essentially benzophenone.

Rearrangement with Antimony Trichloride.—When benzophenoneoxime is added in small portions to the antimony trichloride warmed just above its melting-point, the oxime dissolves to a clear solution with but a trace of color. The addition of each portion of oxime produces a hissing sound, and if a large quantity of oxime is added at once, the reaction becomes violent and the product dark-colored.

On slowly adding 1.8 grams of oxime to 6 grams of trichloride, washing the product with a mixture of alcohol and dilute hydrochloric acid and recrystallizing the residue from alcohol, a yield of 1.5 grams of pure benzanilide is obtained.

SHEFFIELD CHEMICAL LABORATORY,
NEW HAVEN, MARCH, 1897.

THE ACTION OF UREA AND PRIMARY AMINES ON MALEIC ANHYDRIDE.

BY FREDERICK L. DUNLAP AND ISAAC K. PHELPS.

In a former article,[1] a method was described by one of us for obtaining imides by the action of urea on the anhydrides of dibasic acids. It was shown that the formation of imides by the interaction of urea and anhydrides was to be explained by the addition of the urea and the anhydrides to form an acid, which when heated, decomposed with the formation of the imide, carbon dioxide and ammonia. These reactions can be shown by the following equations:

[1] This JOURNAL, 18, 332.

$$R''<\begin{matrix}CO\\CO\end{matrix}>O + NH_2CONH_2 = R''<\begin{matrix}CONHCONH_2\\COOH\end{matrix}$$

$$R''<\begin{matrix}CONHCONH_2\\COOH\end{matrix} = R<\begin{matrix}CO\\CO\end{matrix}>NH + CO_2 + NH_3.$$

In some cases this intermediate product, formed by the addition of the reacting substances, was readily isolated, and upon heating to certain temperatures, it was found that this addition-product decomposed with the formation of the imide.

It was found, in particular, that maleïc anhydride formed an addition-product with urea, and we hoped to obtain the unknown imide of maleïc acid by the decomposition of this addition-product.

Maleüric Acid.—When equal molecules of maleïc anhydride and urea are heated to 100°–105° in an oil-bath, the mixture melts, and if this temperature is maintained for a short time, the liquid solidifies. This product was purified by crystallization from alcohol, and when pure was perfectly white and melted at 167°.5–168° with decomposition. Upon analysis the following results were obtained :

0.2148 gram substance gave 0.2968 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_5H_6O_4N_2$.	Found.
C	37.97	37.69
H	3.80	3.88

Maleüric acid is soluble in hot water and alcohol, fairly insoluble in cold and insoluble in chloroform, benzene, ligroïn, carbon disulphide, acetone, and ether.

Its formation and structure are shown in the following equation :

$$\begin{matrix}H-C-CO\\ \|\\ H-C-CO\end{matrix}\!\!>O + NH_2CONH_2 = \begin{matrix}H-C-CONHCONH_2\\ \|\\ H-C-COOH.\end{matrix}$$

No difficulty was expected in the formation of the imide of maleïc acid, either from the maleüric acid, or by the direct heating of maleïc anhydride and urea ; for, in the cases already studied,[1] the reaction ran with great smoothness and ease. But, for some unknown reason, the imide of maleïc

[1] *Loc. cit.*

acid could not be obtained—at least in quantities for complete identification. A great many experiments were carried out under varying conditions, but only under one set of conditions could any product be isolated, and then unfortunately the yield was so distressingly small that the study of the compound had to be abandoned. When equal molecules of maleïc anhydride and urea are heated in a boiling-flask, at first slowly, and finally at the full heat of a Bunsen burner, a vigorous evolution of carbon dioxide and ammonia took place, and a small amount of a dark-colored distillate was obtained, which on cooling solidified and gave a melting-point of 130°.5 after crystallation from anhydrous acetone. This same crystalline product was also obtained on distilling the maleüric acid. In both cases a large amount of carbonaceous residue remained in the boiling-flask.

Although the method of formation of this compound is exactly parallel to that employed in the preparation of succinimide,[1] yet the identity of this product cannot be regarded as established until sufficient quantities of it have been prepared to subject it to elementary analysis.

The Action of Primary Amines on Maleïc Anhydride.

Anschütz[2] in 1889 published a method by which anilic acids could be very easily prepared by dissolving molecular quantities of aniline and the anhydride of dibasic acids in dry chloroform, when after standing for a short time the anilic acid crystallized out. Following out this line and method of formation, suggested by Anschütz's work, some derivatives of maleïc acid has been prepared and studied.

p-Tolylmaleämic Acid.—Molecular proportions of maleïc anhydride and *p*-toluidine were dissolved in dry chloroform, and upon mixing these two solutions, there immediately separated out a light yellow precipitate. After standing for a time to insure the complete precipitation of the product, it was filtered off and purified by crystallization from alcohol, from which it separated in lemon-yellow needles. The pure product melted at 201°, with evolution of gas. It is readily soluble in ether, acetone and hot alcohol, but insoluble in benzene, ligroïn,

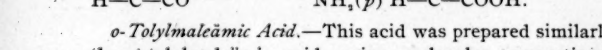
[1] *Loc. cit.* [2] Ber. d. chem. Ges., **20**, 3214.

carbon disulphide, chloroform and water. Upon analysis the following results were obtained :

0.2072 gram substance gave 0.4881 gram CO_2, and 0.1068 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.24
H	5.37	5.73

The structure and mode of formation of this *p*-tolylmaleämic acid may be seen from the following equation :

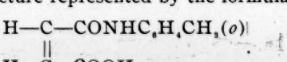


o-Tolylmaleämic Acid.—This acid was prepared similarly to the *p*-tolylmaleämic acid, using molecular proportions of maleïc anhydride and *o*-toluidine. The product was purified by crystallization from alcohol, from which it separated in bunches of thick light yellow prisms. When pure it melted at 117°.5–118°. It is readily soluble in acetone, and in alcohol ; sparingly soluble in chloroform, and insoluble in ligroïn, carbon disulphide, benzene, water, and ether. Analysis gave the following results :

0.2124 gram substance gave 0.4993 gram CO_2, and 0.1146 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.12
H	5.37	5.99

It has the structure represented by the formula



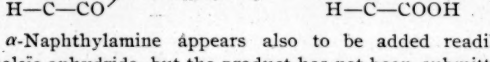
β-Naphthylmaleämic Acid.—When molecular quantities of *β*-naphthylamine and maleïc anhydride were mixed in dry chloroform solution they reacted and united as readily as did the *o*- and *p*-toluidines and the anhydride. Almost immediately a yellow crystalline precipitate separated out. This, after standing a short time, was filtered off and crystallized from alcohol. It separated from alcohol in small bright yel-

low needles, which, when pure, melted at 200° with evolution of gas. It is soluble in acetone and alcohol, but insoluble in ether, carbon disulphide, chloroform, benzene, ligroïn, and water. Analysis gave the following results:

0.2033 gram substance gave 0.5226 gram CO_2 and 0.0948 gram H_2O.

	Calculated for $C_{14}H_{11}O_2N$.	Found.
C	69.71	70.11
H	4.56	5.18

This addition-product is obviously formed as follows:



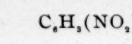
α-Naphthylamine appears also to be added readily to maleïc anhydride, but the product has not been submitted to analysis.

THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY,
MARCH 8, 1897.

ON THE ISOMERIC CHLORIDES OF *p*-NITRO-*o*-SULPHOBENZOIC ACID.

BY IRA REMSEN AND G. W. GRAY.

The interesting results obtained in the investigation[1] of the chlorides of orthosulphobenzoic acid carried out in this laboratory led to the desire to learn whether a substituted orthosulphobenzoic acid would yield two isomeric chlorides corresponding to those obtained from the unsubstituted acid. As one of the nitro derivatives can be obtained comparatively easily, the action of phosphorus pentachloride upon this was first studied. After a number of obstacles had been overcome, we finally succeeded in finding a method by which it is possible to make both the acid chlorides hoped for, that is to say, the symmetrical chloride of the formula,



and the unsymmetrical of the formula

[1] This JOURNAL, **17**, 309, 311, 330, 347; and **18**, 791, 794, 809, 818.

$$C_6H_3(NO_2)\begin{cases}CCl_2\\ \\ SO_2\end{cases}>O.$$

Both are well characterized substances, and both undergo characteristic transformations under the influence of various reagents. The symmetrical compound, when treated with ammonia, gives the ammonium salt of the corresponding sulphinide thus :

$$C_6H_3(NO_2)\begin{cases}COCl\\ \\ SO_2Cl\end{cases} + 2NH_3 = C_6H_3(NO_2)\begin{cases}CO\\ \\ SO_2\end{cases}>NNH_4 + 2HCl.$$

While the unsymmetrical compound gives the ammonium salt of the corresponding cyansulphonic acid thus :

$$C_6H_3(NO_2)\begin{cases}CCl_2\\ \\ SO_2\end{cases}>O + 2NH_3 = C_6H_3(NO_2)\begin{cases}CN\\ \\ SO_2ONH_4\end{cases} + 2HCl.$$

Experimental.

The starting-point in the experiments described below was *p*-nitrotoluene. This was treated with fuming sulphuric acid, and thus converted into *p*-nitro-(*o*)-toluene sulphonic acid. The latter was then oxidized with potassium permanganate, and thus changed to *p*-nitro-(*o*)-sulphobenzoic acid, which was easily obtained in the form of the acid potassium salt,

$$C_6H_2\begin{cases}COOH\\ SO_2OK\,(o).\\ NO_2\,(p)\end{cases}$$

Action of Phosphorus Pentachloride on the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid.—40 grams of the acid potassium salt are mixed with 60 grams of phosphorus pentachloride, and heated in a distilling-bulb at a temperature of 150°. The distilling-bulb is immersed in a sulphuric-acid bath, and kept at a temperature of 150° for four or five hours. Reaction takes place with the formation of the two chlorides.

The yield of the unsymmetrical chloride appears to be from 80

to 90 per cent. and that of the symmetrical from 10 to 20 per cent. The chlorides must not be heated much above 150°, as decomposition begins at 170°. The yield of the second can be increased to about 30 per cent. by heating in an open dish upon the water-bath. The oily mass is poured into water and washed free from phosphorus oxychloride and potassium chloride. The chlorides are then dissolved in chloroform, and the chloroform solution dried by means of calcium chloride. After filtering off the calcium chloride the solution is allowed to evaporate slowly under a bell-jar free from moist air. From this solution a considerable quantity of the solid (symmetrical) chloride is obtained in crystals which look as if they consisted of monoclinic (?) pinacoids and basal plane. The crystals are filtered off and washed with ice-cold chloroform. After no more crystals can be obtained by this method, more chloroform is added and the solution transferred to an Erlenmeyer flask. This flask is immersed in a freezing-mixture of salt and ice, and dry air drawn over the solution for several days. From this more crystals of the symmetrical chloride, mixed with some of the unsymmetrical, are obtained. These are filtered off and washed very quickly with cold chloroform. This dissolves the unsymmetrical chloride with only a very small quantity of the symmetrical chloride. The chloroform solution was evaporated until all the chloroform had been driven off, and the oil was then dissolved in a large volume of petroleum ether (boiling-point 55°–90°). As the ether solution cools it becomes cloudy and then begins to clear up. When this happens, pour the solution into another beaker and allow the solution to cool. From this solution the unsymmetrical chloride then crystallizes in almost pure condition.

This (unsymmetrical) chloride is slightly soluble in petroleum ether, about 1 part in 200, and from this solvent it crystallizes in fine white needles or long flat plates about 3 to 4 mm. broad and 2 to 3 cm. long. They are extremely soluble in ether and chloroform, but crystals cannot be obtained from these solvents. It is decomposed on heating above 160° and

melts at 56°–57° (uncorr.). This chloride is probably identical with that obtained by Kastle.[1]

The symmetrical chloride can be obtained pure by recrystallizing the first crystals obtained above. It can also be obtained by dissolving the two chlorides in chloroform and shaking the solution with dilute ammonia. The ammonia acts immediately upon the unsymmetrical chloride, and only slightly upon the symmetrical. The chloroform solution is washed with water to free it from ammonia, dried by means of calcium chloride, and allowed to evaporate. From the chloroform solution beautiful crystals are obtained, as above described. It is soluble also in ether, but less so than the unsymmetrical chloride. It melts at 94°–95° (uncorr.) It can be heated in a sealed tube at 150° with phosphorus oxychloride without undergoing any decomposition. Both chlorides, when in crystalline form, can be left exposed to moist air without undergoing very much decomposition. When the chlorides are first formed—before crystals are obtained—decomposition goes on more readily, judging by the amount of hydrochloric acid given off.

Portions of both chlorides were heated in a sealed tube with fuming nitric acid. The results obtained were as follows:

0.1933 gram unsymmetrical chloride gave 0.1963 gram AgCl.

0.1933 gram unsymmetrical chloride gave 0.1585 gram $BaSO_4$.

0.1927 gram unsymmetrical chloride gave 0.1950 gram AgCl.

0.1927 gram unsymmetrical chloride gave 0.1548 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}CCl_2\\SO_2\\NO_2\end{cases}>O$.	Found. I.	II.
Cl	24.97	25.00	25.02
S	11.25	11.28	11.06

The symmetrical chloride on analysis gave:

0.1901 gram symmetrical chloride gave 0.1935 gram AgCl.

[1] This JOURNAL, 11, 180.

0.1850 gram symmetrical chloride gave 0.1875 gram AgCl.

	Calculated for $C_6H_3\begin{cases}COCl\\SO_2Cl.\\NO_2\end{cases}$	Found. I.	II.
Cl	24.97	25.15	25.06

Action of Water on the Chlorides.—Cold water acts very slowly upon the chlorides. Even after several months the decomposition is incomplete. In hot water they are not readily decomposed, but, on boiling, the decomposition is complete in a few minutes. The decomposition is about as rapid in one case as in the other. With dilute caustic potash they are readily decomposed, and, after cooling, the addition of an excess of hydrochloric acid causes the appearance of the characteristic acid potassium salt of paranitroorthosulphobenzoic acid from each, thus showing that both yield the same product.

Action of Ammonia upon the Chlorides.—Kastle[1] mentions a product of the action of ammonia upon the chloride, but gives no description of it. It was therefore thought best to repeat this work. Five grams of the symmetrical chloride were dissolved in ether, and poured into a beaker containing 150 cc. of dilute ammonia. The solution was allowed to stand for several days until the ether had evaporated. From this solution the ammonium salt of paranitrobenzoic sulphinide was obtained. The yield is theoretical. The crystals are rectangular plates of glistening flakes, which do not melt below the boiling point of sulphuric acid. It is also soluble in alcohol. On adding hydrochloric acid to this salt paranitrobenzoic sulphinide is obtained. The sulphinide[2] crystallizes in fine needles or plates and melts at 209° (uncorr.).

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 4NH_3 = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4 + 2NH_4Cl;$$

$$C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4 + HCl = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NH + NH_4Cl.$$

When the perfectly dry chloride is dissolved in anhydrous

[1] This JOURNAL, 11, 181. [2] Noyes: This JOURNAL, 8, 170.

ether and dry ammonia gas passed into the solution the same product is obtained.

0.300 gram of this salt gave 0.05147 gram N.
0.300 gram of this salt gave 0.05178 gram N.

	Calculated for $C_6H_3\begin{cases}CO\\SO_3\\NO_2\end{cases}>N.NH_4$.	Found. I.	II.
N	17.18	17.16	17.26

Five grams of the unsymmetrical chloride were dissolved in ether and poured into a beaker containing 100 cc. of dilute ammonia. After the ether had evaporated, nothing crystallized from the solution until it had evaporated to about 50 cc. when a large mass of needles was obtained. These needles grouped themselves in radiating masses or tufts. This product proved to be the ammonium salt of paranitrocyanbenzenesulphonic acid. This salt is also obtained when the mixed chlorides are dissolved in chloroform and shaken with dilute ammonia. From the ammoniacal solution the ammonium salt is obtained on evaporation. From the chloroform solution the symmetrical chloride is obtained.

When ammonia is poured upon the unsymmetrical chloride, solution takes place immediately. In the case of the symmetrical chloride solution is not complete even after twenty-four hours.

The analysis of this salt gave the following results:

0.9965 gram lost over sulphuric acid 0.0687 gram H_2O.

	Calculated for $C_6H_3\begin{cases}CN\\SO_3ONH_4\\NO_2\end{cases}+H_2O$.	Found.
H_2O	6.85	6.90

0.3000 gram of the anhydrous salt gave 0.05148 gram N.
0.3000 gram of the anhydrous salt gave 0.05196 gram N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_3ONH_4\\NO_2\end{cases}$.	Found. I.	II.
N	17.18	17.16	17.32

All nitrogen determinations, which are given in grams, were made by the Kjeldahl method, all others by the absolute method. On adding acid to this salt nothing separated out,

even on boiling. As further study was desirable in order to place the formation of this salt beyond doubt, a number of salts derived from these two ammonium salts were made. In order to facilitate their comparison the isomeric salts are described under the same heading.

The Silver Salts.

Silver Paranitrocyanbenzenesulphonate, $C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases} + H_2O$.—To the hot solution of ammonium paranitrocyanbenzenesulphonate, silver nitrate is added. On cooling, the silver salt crystallizes in fine long rectangular needles 2 cm. long. It contains 1 molecule of water of crystallization, which it loses at 100°.

9.6744 gram of this salt lost 0.0354 gram of H_2O at 100°.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases} + H_2O$.	Found.
H_2O	5.25	5.10

The anhydrous salt on analysis gave the following results:

0.1779 gram gave 0.0760 gram AgCl.

0.1556 gram gave 0.0667 gram AgCl.

0.2010 gram gave 15.1 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases}$.	Found. I.	Found. II.
Ag	32.21	32.16	32.26
N	8.38	8.63	....

Silver Salt of the Sulphinide, $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NAg$.—This salt was prepared by Noyes[1] by adding silver nitrate to the ammonium salt of the sulphinide. It crystallizes from boiling water (1 part in a 1000) in short fine needles. It is difficultly soluble in boiling water, insoluble in cold. It contains no water of crystallization. It turns brown on exposure to the light.

0.1508 gram gave 0.0645 gram AgCl.

0.1995 gram gave 0.0856 gram AgCl.

[1] This JOURNAL, 8, 172.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.Ag.$	Found. I.	II.
Ag	32.21	32.20	32.30

The Potassium Salts.

Potassium Paranitrocyanbenzenesulphonate, $C_6H_3\begin{cases}CN\\SO_2OK+\\NO_2\end{cases}$ $1\frac{1}{2}H_2O$.—This salt is prepared by treating the silver salt with sufficient potassium chloride to precipitate all the silver. The solution is filtered from the silver chloride and evaporated to crystallization. The potassium salt crystallizes in beautiful colorless needles 2 to 3 cm. in length, and contains $1\frac{1}{2}$ molecules of water of crystallization.

9.3177 gram lost 0.0287 gram H_2O at 100°.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OK+1\frac{1}{2}H_2O.\\NO_2\end{cases}$	Found.
H_2O	9.21	9.03

0.1868 gram anhydrous salt gave 0.0605 gram K_2SO_4.

0.2495 gram anhydrous salt gave 0.0802 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OK.\\NO_2\end{cases}$	Found. I.	II.
K	14.66	14.54	14.43

Potassium Salt of the Sulphinide,[1] $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NK.$—This salt was prepared by treating paranitrobenzoic sulphinide with potassium carbonate to neutral reaction. It crystallizes in fine leaflets and contains no water of crystallization. It is easily soluble in hot water, but difficultly soluble in cold.

0.2352 gram of this salt gave 0.0757 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2>NK.\\NO_2\end{cases}$	Found.
K	14.66	14.45

[1] Noyes: *Loc cit.*, **8**, 170.

The Barium Salts.

Barium Paranitrocyanbenzenesulphonate, $\left(C_6H_2\begin{cases}CN\\SO_3O\\NO_2\end{cases}\right)_2Ba + 2\frac{1}{2}H_2O$.—This salt is made by treating the silver salt with barium chloride. It could not be obtained in well-formed crystals, but formed wart-like masses. It is readily soluble in cold water, and contains $2\frac{1}{2}$ molecules of water of crystallization.

0.3747 gram of this salt lost 0.0265 gram H_2O at 100°.

0.3698 gram of this salt gave 0.1325 gram $BaSO_4$.

	Calculated for $\left(C_6H_2\begin{cases}CN\\SO_3O\\NO_2\end{cases}\right)_2Ba + 2\frac{1}{2}H_2O$.	
H_2O	7.07	7.07
Ba	21.08	21.23

It loses $1\frac{1}{2}$ molecules of water of crystallization over sulphuric acid.

0.2093 gram anhydrous salt gave 0.0822 gram $BaSO_4$.

	Calculated for $\left(C_6H_2\begin{cases}CN\\SO_3O\\NO_2\end{cases}\right)_2Ba$.	
Ba	23.17	23.09

Barium Salt of the Sulphinide,[1] $\left(C_6H_2\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba + 3H_2O$.—This salt is obtained by treating the sulphinide with barium carbonate. The solution is filtered from the excess of barium carbonate and allowed to crystallize. It forms well developed prisms which contain 3 molecules of water of crystallization.

0.3881 gram of this salt lost 0.0329 gram H_2O at 100°.

	Calculated for $\left(C_6H_2\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba + 3H_2O$.	Found.
H_2O	8.37	8.44

[1] Noyes: This JOURNAL, 8, 171.

0.3552 gram of the anhydrous salt gave 0.1396 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\end{matrix}\right.>N\right)_2Ba$.	Found.
Ba	23.17	23.10

The Calcium Salts.

Calcium Paranitrocyanbenzenesulphonate, $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ca + 7H_2O$.—This is formed by treating the silver salt with calcium chloride. It is extremely soluble in water. It is, in fact, soluble in less than its own weight of water. It forms flat elongated plates. It loses 3 molecules of water of crystallization over sulphuric acid and 4 more at 135°.

0.6459 gram lost 0.0543 gram H_2O over sulphuric acid.

0.6459 gram lost 0.1294 gram H_2O at 135°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ca + 7H_2O$.	Found.
$7H_2O$	20.31	20.04

0.2429 gram anhydrous salt gave 0.0661 gram $CaSO_4$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ca$.	Found.
Ca	8.09	8.00

Calcium Salt of the Sulphinide, $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Ca + 6H_2O$.—This is formed by treating paranitrobenzoic sulphinide with calcium carbonate. It forms long, transparent, rectangular columns, which soon lose part of their water of crystallization and become opaque.

0.7069 gram of this salt lost 0.1272 gram water at 100°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Ca + 6H_2O$.	Found.
$6H_2O$	17.93	17.98

0.1013 gram anhydrous salt gave 0.0526 gram $CaSO_4$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_3\\NO_2\end{matrix}\right.>N\right)_2Ca$.	Found.
Ca	8.09	8.09

The Magnesium Salts.

Magnesium Paranitrocyanbenzenesulphonate, $\left(C_6H_3\left\{\begin{matrix}CN\\SO_3O\\NO_2\end{matrix}\right.\right)_2Mg + 8H_2O$.—This salt is formed by treating the silver salt with magnesium chloride. It crystallizes in prisms which are somewhat elongated. It is extremely soluble in water and contains 8 molecules of water of crystallization: of these it loses $3\frac{1}{2}$ molecules over sulphuric acid.

0.3800 gram of this salt lost 0.0494 gram H_2O over sulphuric acid.

0.3800 gram of this salt lost 0.0882 gram H_2O at 200°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CH\\SO_3O\\NO_2\end{matrix}\right.\right)_2Mg + 8H_2O$.	Found.
$3\frac{1}{2}H_2O$	13.01	13.00
$8\ H_2O$	23.12	23.21

0.1695 gram of the anhydrous salt gave 0.0411 gram $Mg_2P_2O_7$.

0.2119 gram of the anhydrous salt gave 0.0493 gram $Mg_2P_2O_7$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_3O\\NO_2\end{matrix}\right.\right)_2Mg$.	Found. I.	Found. II.
Mg	5.09	5.31	5.09

Magnesium Salt of the Sulphinide, $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Mg + 6\frac{1}{2}H_2O$.—This is formed by treating paranitrobenzoic sulphinide with magnesium carbonate. The salt forms beautiful transparent crystals, which seem to be a combination of orthorhombic (?) domes and prisms. These crystals soon lose their lustre and become opaque. The salt contains 6.5 molecules of water of crystallization.

0.2682 gram of this salt lost 0.0527 gram H_2O at 180°.

1.2834 gram of this salt lost 0.2570 gram H_2O at 180°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right)_2Mg + 6\frac{1}{2}H_2O$.	Found. I.	Found. II.
$6\frac{1}{2}H_2O$	19.64	19.60	19.97

0.2165 gram of the anhydrous salt gave 0.0523 gram $Mg_2P_2O_7$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right)_2Mg$.	Found.
Mg	5.09	5.29

Zinc Salts.

Zinc Paranitrocyanbenzenesulphonate, $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Zn + 7H_2O$.—This is formed when the silver salt is treated with zinc chloride. It forms long prismatic columns, is extremely soluble in water, and contains 7 molecules of water of crystallization.

0.7453 gram of this salt lost 0.1477 gram H_2O at 170°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Zn + 7H_2O$.	Found.
$7H_2O$	19.52	19.82

0.2064 gram anhydrous salt gave 0.0318 gram ZnO.

0.1700 gram anhydrous salt gave 0.0264 gram ZnO.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Zn$.	Found. I.	Found. II.
Zn	12.60	12.38	12.48

Zinc Salt of the Sulphinide, $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right)_2Zn + 4\frac{1}{2}H_2O$.—This is formed by treating paranitrobenzoic sulphinide with zinc carbonate. It forms short thick prisms combined with domes, and resembles very much the corresponding magnesium salt. It contains 4.5 molecules of water of crystallization.

0.1861 gram of this salt lost 0.0254 gram H_2O at 125°.

0.4327 gram of this salt lost 0.0593 gram H_2O at 125°.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Zn+4\frac{1}{2}H_2O$.	Found. I.	Found. II.
$4\frac{1}{2}H_2O$	13.49	13.65	13.71

0.2102 gram of the anhydrous salt gave 0.0328 gram ZnO.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Zn$.	Found.
Zn	12.60	12.54

The Ethereal Salts.

The Methyl Salt of the Sulphinide, $C_6H_3\begin{cases}CO\\SO_2>N.CH_3\\NO_2\end{cases}$.—This salt is formed by heating the silver salt of paranitrobenzoic sulphinide in a sealed tube at 100° with methyl iodide. The methyl salt is extracted with boiling alcohol. On cooling, it crystallizes in leaf-like crystals. It is readily soluble in hot alcohol, but difficultly soluble in cold alcohol. It is also soluble in water. It melts at 179° (uncorr.).

0.1575 gram of this salt gave 14.73 cc. N.

0.1561 gram of this salt gave 14.25 cc. N.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2>NCH_3\\NO_2\end{cases}$.	Found. I.	Found. II.
N	11.59	11.77	11.49

From the product of the action of methyl iodide upon the silver salt of paranitrocyanbenzenesulphonic acid nothing definite has been obtained.

The Ethyl Salt of the Sulphinide, $C_6H_3\begin{cases}CO\\SO_2>NC_2H_5\\NO_2\end{cases}$.—This salt is formed when the silver salt of the sulphinide is heated in a sealed tube at 100° with ethyl iodide. The mass is extracted with boiling alcohol, filtered, and allowed to cool, when a mass of needles resembling dinitrobenzene is obtained. It is readily soluble in hot alcohol, but difficulty soluble in cold alcohol; it is also soluble in water. It melts at 172° (uncorr.).

0.1509 gram of this salt gave 13.53 cc. N.

0.1645 gram of this salt gave 14.68 cc. N.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NC_2H_5$.	Found. I.	II.
N	10.97	11.26	11.21

From the silver salt of paranitrocyanbenzenesulphonic acid we have been unable to obtain an ethereal salt by the action of ethyl iodide, but have obtained a substance which is strongly acid, the nature of which has not yet been determined. It is probably analogous to the orthobenzaminesulphonic acid obtained by Jesurun[1] by the action of alcohol on orthocyanbenzenesulphonic acid.

The reactions are probably those given below:

$$C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases} + C_2H_5I = C_6H_3\begin{cases}CN\\SO_2OC_2H_5\\NO_2\end{cases} + AgI.$$

$$C_6H_3\begin{cases}CN\\SO_2OC_2H_5\\NO_2\end{cases} + C_2H_5OH + H_2O = C_6H_3\begin{cases}CONH_2\\SO_2OH\\NO_2\end{cases} + (C_2H_5)_2O.$$

Paranitrocyanbenzenesulphonic Acid, $C_6H_3\begin{cases}CN\\SO_2OH\\NO_2\end{cases} + H_2O$.

This acid is formed when its silver salt is treated with enough hydrochloric acid to precipitate all the silver, and also by treating the barium salt with sulphuric acid. The acid crystallizes in long prisms, which contain 1 molecule of water of crystallization. If heated rapidly it melts between 145° and 150°, but solidifies again immediately. This is due to the fact that the acid dissolves in its water of crystallization, and when this is driven off it solidifies. It is soluble in less than its own weight of water. On heating the acid with caustic potash for some time, ammonia is liberated, and then on adding an excess of hydrochloric acid a mass of fine needles resembling the acid potassium salt of paranitroorthosulphobenzoic acid is obtained. When the acid is heated to 130° it loses 1 molecule of water and, if the temperature is then raised to 150°, it begins to increase in

[1] Ber. d. chem. Ges., 26, 2287.

weight. This increase is probably due to a change in the cyanogen group.

0.3603 gram of the acid lost 0.0254 gram H_2O at 130°.

0.2503 gram of the acid gave 0.2861 gram N.

0.3033 gram of the acid gave 0.03403 gram N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_3OH\\NO_2\end{cases} + H_2O$.	Found. I.	II.
H_2O	7.31	7.06	....
N	11.42	11.43	11.23

Paranitrocyanbenzenesulphone Chloride, $C_6H_3\begin{cases}CN\\SO_2Cl\\NO_2\end{cases}$.—The chloride is formed when the potassium salt of paranitrocyanbenzenesulphonic acid is treated with phosphorus pentachloride. One molecule of potassium salt is mixed with one molecule of phosphorus pentachloride, and the mixture heated to 140° in a sulphuric-acid bath for several hours. The mass is then treated with water to decompose the phosphorus oxychloride, and to dissolve the potassium chloride. The chloride is then dissolved in chloroform, and dried by means of calcium chloride. When the chloroform solution is allowed to evaporate, the chloride crystallizes in long rectangular prisms, which melt at 107°–108° (uncorr.). They are soluble in chloroform, ether, and benzene.

0.2640 gram of this chloride gave 0.2538 gram $BaSO_4$.

0.1640 gram of this chloride gave 0.1572 gram $BaSO_4$.

0.2025 gram of this chloride gave 18.75 cc. N.

0.1640 gram of this chloride gave 0.0984 gram AgCl.

0.2640 gram of this chloride gave 0.1544 gram AgCl.

0.1003 gram of this chloride gave 0.0592 gram AgCl.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2Cl\\NO_2\end{cases}$.	Found. I.	II.	III.
Cl	14.38	14.83	14.46	14.59
N	11.40	11.63	....	....
S	13.00	13.23	13.19	....

Paranitrocyanbenzenesulphonamide, $C_6H_3\begin{cases}CN\\SO_2NH_2\\NO_2\end{cases}$. — The

amide is formed when paranitrocyanbenzenesulphone chloride is treated with ammonia. 2 grams of the chloride were dissolved in chloroform and added to an aqueous solution of ammonia. The mixture was shaken in a separating-funnel occasionally. The amide separated as an amorphous mass. This was filtered off and recrystallized from alcohol. It crystallized in small rectangular blocks resembling cane sugar. It does not melt below 270°. The yield is theoretical.

0.1920 gram of this salt gave 28.02 cc. N.

0.1535 gram of this substance gave 22.79 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2NH_2\\NO_2\end{cases}$.	Found. I.	Found. II.
N	18.33	18.54	18.65

Paranitrocyanbenzenesulphonanilide, $C_6H_3\begin{cases}CN\\SO_2NHC_6H_5\\NO_2\end{cases}$.—The anilide is formed in the same way as the amide. Dissolve 1 gram of the chloride in chloroform, and add aniline suspended in water. Heat the solution to drive off the chloroform. As the chloroform is evaporated, the anilide separates as a powder. This powder is recrystallized from alcohol. The yield is theoretical. The anilide crystallizes in fine needles and melts at 207°–208° (uncorr.)

0.1513 gram of this anilide gave 16.97 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2NHC_6H_5\\NO_2\end{cases}$.	Found.
N	13.94	14.09

The action of aniline and of the toluidines upon the two chlorides was studied to a sufficient extent to show that isomeric anilides and toluides are formed as in the case of the two chlorides of orthosulphobenzoic acid. These products have, however, since been studied more thoroughly by Mr. W. E. Henderson, in this laboratory, and he will publish his results later.

JOHNS HOPKINS UNIVERSITY,
JUNE, 1895.

A STUDY OF FERRIC HYDROXIDE IN PRECIPITATION.

By Vernon J. Hall.

The tendency of many precipitates to carry other substances into precipitation with them is well recognized. Practical illustrations of this are seen in the use of aluminium hydroxide in mordanting and in freeing polluted water of organic matter.

In quantitative analysis it is the cause of much inconvenience, as will be seen from a statement of Fresenius upon the precipitation of ferric hydroxide by an alkali: "If the precipitant alkali is not used in excess, the precipitate contains basic salt; on the other hand, if the alkali has been used in excess, a portion of it is invariably carried down in combination with the ferric hydroxide." In general, it may be said that this tendency is especially characteristic of the metallic hydroxides. However, that it is not limited to gelatinous precipitates is seen in the marked tendency of barium sulphate to carry substances into precipitation, notably barium chloride and iron. In an investigation by A. V. E. Young upon the "Thermo-chemical Reaction between Alum and Potassium Hydrate,"[1] results were obtained which contradicted the theory of cohesion or "mechanical inclusion" as an adequate explanation of this peculiar phenomenon, and warranted a refutation of the equation ordinarily used to represent the true reaction between aluminium sulphate and potassium, hydroxide, *viz.*:

$$Al_2(SO_4)_3 + K_2SO_4 + 6KOH = 4K_2SO_4 + Al_2(OH)_6.$$

For the purpose of ascertaining if these same facts are true concerning other precipitates closely related in nature to aluminium hydroxide, I have studied the precipitation of ferric hydroxide with reference to its effect upon potassium sulphate. The reaction studied is ordinarily expressed by the following equation:

$$Fe_2Cl_6 + 6KOH + 4K_2SO_4 = Fe_2(OH)_6 + 6KCl + 4K_2SO_4.$$

The results of the work will show that this equation does

[1] This Journal, 8, 23.

not completely represent the reaction. As in the case of aluminium they show the "mechanical inclusion" theory inadequate, and point toward a phenomenon of a strictly chemical nature.

Solutions.

I made the solutions for the work as follows:

(1) A dilute solution of potassium hydroxide standardized by titration against oxalic acid as well as gravimetrically.

(2) A dilute solution of sulphuric acid standardized by titration against the potassium hydroxide solution. It was very important that the exact content of these solutions should be known, so, in addition to the titrations, I made gravimetric determinations of the potassium sulphate introduced into each system.

(3) A solution of ferric chloride made by dissolving 11.2 grams of pure iron wire in hydrochloric acid, evaporating the excess, oxidizing with nitric acid, and making up to a liter with water (Temperature 18½° C.). Care was taken that all the nitric acid was expelled, as the determination of barium sulphate in the presence of even small quantities of nitric acid is unsatisfactory.

General Method.

Since washing changes the composition of the precipitate, I analyzed the filtrates, and subtracted the quantities of each constituent found from the total introduced. This method has been followed throughout the work.

Series I.

The first point to be determined was whether or not sulphur trioxide or potassium oxide were carried down when potassium hydroxide was added in the proportion of six molecules. With this in view I made up a system as follows: Into a 500 cc. flask, the same used throughout the work in all volumetric measurements, I introduced sulphuric acid and then exactly neutralized this with potassium hydroxide, making a quantity of potassium sulphate equivalent to four molecules. To this I added 50 cc. of ferric chloride solution; then potassium hydroxide, equivalent to six molecules; and finally enough

more to neutralize the free acid of the ferric chloride solution. The quantity necessary for this was determined as follows: To 50 cc. of the ferric chloride solution I added potassium hydroxide to alkaline reaction, using phenolphthalein as an indicator. This gave the total acid in the solution. Knowing the quantity of the iron in 50 cc., I calculated how much potassium hydroxide was needed to be in the proportion of six molecules to one of ferric chloride. This quantity, subtracted from that necessary for alkaline reaction, gave the quantity equivalent to the free acid in the ferric chloride solution.

The system already constituted according to the equation before indicated, was made up to 500 cc. with water (Temperature 18½° C.). Of this mixture, well stirred, I drew off 200 cc. into the original 500 cc. flask, dissolved the precipitate by hydrochloric acid, and reprecipitated, while warm, with ammonium hydroxide.

After boiling vigorously for fifteen or twenty minutes with an excess of ammonium hydroxide present, the mixture was cooled and made up to 500 cc. (Temperature 18½° C.). It was then thrown upon a dry filter, received into a dry flask and labeled "Total" for subsequent determination of total sulphur trioxide and potassium oxide in the system. I assumed that this operation liberated any sulphur trioxide and potassium oxide carried down in the first precipitation of ferric hydroxide. That this assumption is true is shown by the constancy of the values for "Totals" in the several systems made up, and still more conclusively by the blank experiments. The latter were made by constituting a system without ferric chloride, but with the same quantities of sulphuric acid and potassium present as in the system already described, and following exactly the same procedure. The following is a comparison of the results:

Mean of twenty-six determinations of sulphur trioxide on "Totals" of twelve different systems, 0.1161 grams per 50 cc. of solution.

Mean of two determinations made on "blanks" in Series I, Experiment 3, 0.1166 gram per 50 cc. of solution. The difference 0.0005 amounts to less than 0.5 per cent. of the quantities measured.

Table—Series I.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	SO_3 in total	SO_3 in filtrate.	SO_3 in precipitate.	K_2O in total.	K_2O in filtrate.	K_2O in precipitate.	Per cent. total Fe_2O_3 in precipitate.	Per cent. total SO_3 in precipitate	Per cent. total K_2O in precipitate.
1	8	.0800	.0000	.0800	.1169, .1167 → .1168	.1178, .1179 → .1179	.0000	.3334	.3311	.0023	100.00	0.00	0.69
2	8	.0800	.0000	.0800	.1164, .1159 → .1161	.1169, .1175 → .1172	.0000	.3338, .3329 → .3333	.3305, .3305 → .3305	.0028	100.00	0.00	0.84
3	6	.0800	.0000	.0800	.1166*, .1166*, .1162, .1161 → .1164	.1168, .1167, .1176, .1172 → .1170	.0000	.2884*, .2879*, .2875, .2883 → .2880	.2867, .2865 → .2866	.0014	100.00	0.00	0.48
4	5	.0800	.0009	.0791	.1164, .1161 → .1163	.1036, .1037 → .1037	.0126	.2629	.2640, .2635 → .2638	.0000	98.8 } 98.9	10.8 } 11.0	0.00
5	5	.0800	.0007	.0793	.1169, .1173 → .1171	.1040, .1038 → .1039	.0132	.2631, .2621 → .2626	.2650, .2640 → .2645	.0000	99.1	11.2	0.00
6	4	.0800	.0108	.0692	.1168, .1176 → .1172	.1027, .1030 → .1029	.0143	.2396, .2396 → .2396	.2404, .2407 → .2406	.0000	86.4 } 84.3	12.2 } 11.5	0.00
7	4	.0800	.0146	.0654	.1159, .1162, .1158 → .1159	.1033, .1030 → .1032	.0127	.2399, .2405 → .2402	.2401, .2399 → .2400	.0000	81.8	10.9	0.00
8	3	.0800	.0308	.0492	.1167, .1167, .1160 → .1165	.1055, .1054, .1052 → .1054	.0111	.2158, .2156 → .2157	.2164, .2164 → .2164	.0000	61.5	9.53	0.00
9	2	.0800	.0511	.0289	.1164, .1165 → .1165	.1097, .1094 → .1096	.0069	.1929, .1923 → .1926	.1923, .1932 → .1928	.0000	36.1	5.92	0.00
10	8	.1600	.0000	.1600	.1161, .1160 → .1161	.1165, .1163 → .1164	.0000	.5229, .5225 → .5227	.5169, .5175 → .5172	.0055	100.00	0.00	1.05
11	5	.1600	.0012	.1587	.1168, .1159 → .1163	.0852, .0854 → .0853	.0310	.3911	.3944	.0000	99.2	26.6	0.00
12	4	.1600	.0335	.1265	.1159, .1153 → .1156	.0881, .0878 → .0880	.0276	.3449	.3460	.0000	79.0	23.9	0.00

* Blanks.

Mean of two determinations of potassium oxide made in Series I, Experiment 3, 0.2879 gram per 50 cc. of solution.

Mean of two determinations made on "blanks" in Series I, Experiment 3, 0.2881 gram per 50 cc. of solution. Here again the difference is inconsiderable, amounting to less than 0.1 per cent. of the quantity measured.

The remainder of the original mixture—solution and precipitate—left in the beaker, was filtered through a dry filter into a dry flask and labeled "Filtrate." Duplicate determinations of sulphur trioxide and potassium oxide were made on this, using 50 cc. for each. The determinations of sulphur trioxide were made according to the ordinary method of precipitating with barium chloride in the presence of free hydrochloric acid and weighing as barium sulphate.

The determinations of potassium oxide were made by evaporating to dryness in a platinum dish with a slight excess of sulphuric acid present, expelling the excess, and igniting the potassium sulphate to constant weight.

Of the "Total" solution, 100 cc. were used for each determination. These were also made in duplicate and in the same manner as in the case of the "Filtrate" solution. It is to be seen that by using 100 cc. of the "Total" for each determination, I obtained results for barium sulphate, which multiplied by 12.5 and divided by 10 became comparable with the quantities in the "Filtrate."

Were the reaction between ferric chloride and potassium hydroxide completely represented by the equation before given, I should obtain the same quantities of sulphur trioxide and potassium oxide in the "Filtrate" as in the "Total," for the potassium sulphate is supposed to take no part whatever in the reaction. The results in Series I, Experiment 3, show that this is not true. They are as follows:

$$\begin{aligned} K_2O \text{ in "Total"} &= 0.2880 \pm 0.0003 \\ K_2O \text{ in "Filtrate"} &= 0.2866 \pm 0.0001 \\ \hline K_2O \text{ in precipitate} &= 0.0014 \pm 0.0004 \end{aligned}$$

$$\begin{aligned} SO_3 \text{ in "Total"} &= 0.1164 \\ SO_3 \text{ in "Filtrate"} &= 0.1170 \\ \hline SO_3 \text{ in precipitate} &= 0.0006 \end{aligned}$$

These results show unmistakably that sulphur trioxide is absent, but that about 0.5 per cent. of the total potassium oxide in the system is present in the precipitate. The quantity is very small as a basis for conclusion, but an examination of the data shows that the probable error is only ± 0.0004.

Using the same quantities of potassium sulphate and ferric chloride as before, I proceeded to precipitate the ferric chloride with five molecules of potassium hydroxide and note the change, if any, in the composition of the ferric hydroxide precipitate. After shaking thoroughly, I made up the mixture to 500 cc. with water (Temperature 18½° C.). The "Totals" were made as before. The "Filtrates" were made as follows: After the ferric hydroxide had been filtered out, I drew off 200 cc. of the filtrate into the 500 cc. flask, boiled with ammonium hydroxide, cooled and made up to volume (Temperature 18½° C.). The ferric hydroxide was then filtered out and determined, and the filtrate received into a dry flask. The need of this slight variation in the method of preparing the "Filtrate" arises from the fact that at five molecules the iron is not completely precipitated, and the remainder must be removed before sulphur trioxide can be determined successfully. It is to be noted, however, that at five molecules the precipitation is very nearly complete, the quantities found in the filtrate being about 1 per cent. of the total quantity of ferric oxide introduced into the system.

A marked change in the composition of the precipitate at this point, as compared with that of six molecules, is to be noted. While at six molecules the sulphur trioxide was undisturbed, and potassium oxide was carried down, on the contrary, at five molecules, 11 per cent. of the total sulphur trioxide present is carried into the precipitate and potassium oxide is undisturbed.

In a subsequent series of experiments I used the same quantities of potassium sulphate and ferric chloride, again only partly precipitating the ferric hydroxide with four, three and two molecules successively. The "Totals" and "Filtrates" were made in the same manner as at five molecules. The results were given in Series I, Experiments 6, 7, 8 and 9. They show a regular decrease in the quantity of sulphur

trioxide in the precipitate, although an increase in proportion to the ferric hydroxide in the same. The differences, however, in the quantities of sulphur trioxide at five and four molecules were so small, and so closely approached the limit of error as to make it uncertain whether these differences were real. I therefore increased the magnitude of the phenomenon by using twice as much ferric chloride and potassium hydroxide, but the same quantity of potassium sulphate. The results, Experiments 11 and 12, show unmistakably a decrease in sulphur trioxide in passing from five to four molecules of potassium hydroxide. They show further that by increasing the ferric hydroxide in the system 100 per cent., the sulphur trioxide is increased 100 per cent. or more.

In addition to the experiments just mentioned, I made two others, using eight molecules of potassium hydroxide. For the results see Experiments 1 and 2. They show the absence of sulphur trioxide and an increase of about 100 per cent. of potassium oxide in the precipitate over that at six molecules. These also are verified by a third in which the phenomenon was increased as just mentioned (See Experiment 10). This again shows that increasing the ferric hydroxide in the system greatly increases the potassium oxide present in the precipitate.

Upon completing the work just described I proceeded to investigate the action of ferric hydroxide upon substances other than potassium sulphate. The following question presented itself for consideration: What will be the action of ferric hydroxide upon potassium chloride, in the system constituted according to the following equation:

$$Fe_2Cl_6 + 6KOH = Fe_2(OH)_6 + 6KCl \ (?)$$

To answer this question, I introduced into systems, each containing a constant quantity of ferric chloride, potassium hydroxide in varying molecular proportions, and, as outlined in the previous work, determined the action of ferric hydroxide upon potassium chloride by differences between "Totals" and "Filtrates." Owing to the fact that chlorine cannot be determined as silver chloride in the presence of ammonium salts, I could not remove the iron by ammonium

hydroxide from the "Totals" and "Filtrates" at points of incomplete precipitation as I have uniformly done heretofore. It was necessary therefore to determine the chlorine in the presence of iron. Whether or not this could be done successfully was the first point considered. For this purpose I made up a solution containing a quantity of chlorine approximately equivalent to the chlorine in the ferric chloride solution. Of this solution I drew off two portions of 50 cc. each for determinations of total chlorine introduced. Also two other portions of 50 cc. each of which I treated as follows: To one portion I added a quantity of iron in the form of a solution of ammonium iron alum, approximately equal to that which would be present in the actual determinations. To another portion I added twice this quantity. The chlorine was determined by the ordinary method of precipitation with silver nitrate and weighing as silver chloride. In washing the silver chloride I found it extremely difficult to wash out all the iron, so in addition to the one-tenth gram of silver nitrate, ordinarily used per liter of wash-water, I added twenty-five cc. concentrated nitric acid. I found that this not only removed all traces of iron from the silver chloride, but in addition served to prevent any decomposition of silver nitrate. That the presence of iron in the given conditions does not interfere in the least with the accurate determination of the chlorine as silver chloride, will be seen from the following results:

	No iron.	Containing iron.	
Solution 1	0.4647	0.4640	0.1 gram.
Solution 2	0.4638	0.4642	0.2 "
	0.4637		
Solution 3	0.4641	0.4637	0.3 "
	0.4636	0.4642	
	0.4639 AgCl	0.4640 AgCl.	

Series II.

The first point considered in the investigation was the action of ferric hydroxide upon potassium chloride at complete precipitation of the ferric hydroxide, that is at six molecules.

I made a system as follows: Into a 500 cc. flask I intro-

Table—Series II.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	Cl in total.	Cl in filtrate.	Cl in precipitate.	Per cent. total Fe_2O_3 in precipitate.	Per cent. total Cl in precipitate
13	6	.0800	.0000	.0800	.1127 / .1127 — .1127	.1133 / .1133 — .1133	.0000	100.00	0.00
14	6	.0800	.0000	.0800	.1127 / .1126 — .1127	.1127 / .1126 — .1127	.0000	100.00	0.00
15	5½	.0800	.0067	.0733	.1127 / .1128 — .1128	.1074 / .1073 — .1074	.0054	91.6	4.79
16	5	.0800	.0191	.0609	.1132 / .1132 — .1132	.1081 / .1082 — .1082	.0050	76.1 } 76.1	4.42 } 4.5
17	5	.0800	.0191	.0609	.1127 / .1125 — .1126	.1074 / .1074 — .1074	.0052	76.1	4.62
18	4	.0800	.0479	.0321	.1127 / .1125 — .1126	.1098 / .1098 — .1098	.0028	40.1	2.49
19	3	.0800	.0567	.0233	.1126 / .1125 — .1126	.1104 / .1105 — .1105	.0021	29.1	1.87

duced 50 cc. of ferric chloride solution and then potassium hydroxide in the proportion of six molecules, and enough more to neutralize the excess of acid in the ferric chloride solution. I made this to volume (18½° C.) with water, stirred thoroughly, and drew off three portions of 50 cc. each, containing ferric hydroxide precipitate. In these, after dissolving the precipitate with nitric acid, I determined the total chlorine in the system. The remainder of the mixture was then thrown upon a dry filter and received into a dry flask. Of this I took two portions of 50 cc. each, and determined the chlorine present in the "Filtrate." For results, see Series II, Experiments 13 and 14. They show clearly that no chlorine is present in the precipitate at six molecules, the "Totals" and "Filtrates" being identical.

Using the same quantity of ferric chloride in each as in the experiment just described, I proceeded to constitute systems with five, four and three molecules of potassium hydroxide, and to observe the change, if any, in the composition of the ferric hydroxide. The method followed was identical with that just given for six molecules, with the addition that I made determinations of the ferric hydroxide present in 50 cc. of the "Filtrate" in every case, in order to compare the quantity actually precipitated with that calculated on the basis of the molecular proportion of potassium hydroxide used.

It will be observed that, although the same quantity of ferric chloride is used throughout, less ferric hydroxide is precipitated at five, four and three molecules in these systems than at the corresponding points when potassium sulphate is present in the system. The probable cause for this is that the basic sulphate of iron formed in the system when potassium sulphate is present is less soluble than the corresponding basic chloride formed when potassium sulphate is absent. It will be seen by reference to Series II, Experiments 15, 16, 17, etc., that the same action on the part of ferric hydroxide is maintained toward chlorine as was manifested toward sulphur trioxide when the latter was present in the system in Series I.

At six molecules the chlorine was undisturbed, the "Totals" and "Filtrates" being identical. At points short of com-

plete precipitation of the ferric hydroxide, however—five and one-half, five, four and three molecules—a marked change in the composition of the precipitate is noted. Further it will be observed that the quantity of chlorine present in the precipitate diminishes in going from five and one-half molecules to five, and so on. From this fact it might be inferred that still more chlorine would be found in the precipitate at points beyond five and one-half molecules; in other words, that the maximum quantity of chlorine would be carried down just short of six molecules.

Series III.

In addition to the series just mentioned, I made another, the object of which was to determine whether or not chlorine is disturbed in systems, such as those in Series I, when potassium sulphate is present. These observations were made at six and five molecules. The method of making the solution and the manner of analysis so far as sulphur trioxide is concerned, were identical with those at corresponding points in Series I, except that 1000 cc. of the solution was made up instead of 500 cc. in order to give sufficient material to work upon. In determining chlorine I drew off three portions of 50 cc. each, of solution containing ferric hydroxide precipitate, in which, after dissolving the precipitate with nitric acid, I determined the total chlorine introduced. For the "Filtrate" I drew off 50 cc. portions of the filtered solution. The results of these experiments are shown in Series III, Experiments 20 and 21. At six molecules neither chlorine nor sulphur trioxide appears in the precipitate. At five molecules, however, 13 per cent. of the total sulphur trioxide is carried down and the chlorine is undisturbed. From this it is evident that whenever potassium sulphate is present the ferric hydroxide acts upon it in preference to the potassium chloride.

Discussion.

How far do the results obtained go toward answering the prime question: Is the presence of these substances in the precipitate due to "mechanical inclusion" (occlusion), or to something of the nature of adhesion, or, finally, is it due to chemical action?

Table—Series III.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	Cl in total.		Cl in filtrate.		Cl in precipitate.	SO_3 in total.		SO_3 in filtrate.		SO_3 in precipitate.	Per cent. total Fe_2O_3 in precipitate.	Per cent. total Cl in precipitate	Per cent. total SO_3 in precipitate
20	6	.0800	.0000	.0800	.1128 .1129	.1129	.1131 .1132	.1132	.0000	.1162 .1161	.1162	.1161 .1156	.1159	.0000	100.00	0.00	0.00
21	5	.0800	.0014	.0786	.1127 .1127	.1127	.1129 .1129	.1129	.0000	.1159 .1151	.1155	.1007 .1004	.1005	.0150	98.2	0.00	13.0
										K_2O		K_2O		K_2O			K_2O
22	6	.2400	.0000	.2400	.3376 .3382	.3379	.3390 .3388	.3389	.0000	.4532		.4512 .4543	.4528	.0000	100.00	0.00	0.00
23	5	.2400	.1112	.1288	.3376 .3378	.3377	.3262 .3262	.3262	.0115	.3773		.3835		.0000	53.7	3.4	0.00

The question may be considered first with respect to sulphur trioxide. In what form has it been carried down? Certainly not as potassium sulphate, as is evident upon a glance at Series I. At six molecules, when potassium oxide appears in the precipitate, sulphur trioxide does not; on the contrary, with five, four, three and two molecules of potassium hydroxide present, sulphur trioxide appears and potassium does not. Were the precipitation made from a solution of ferric sulphate, there might be reason to think that sulphur trioxide appeared in the precipitate as a residue, so to speak, from the ferric sulphate, but the use of ferric chloride instead of ferric sulphate is assumed to remove all such possibility.

It may be claimed, however, that upon mixing ferric chloride and potassium sulphate, ferric sulphate is formed. That the sulphur trioxide in the precipitate is not dependent upon the formation of ferric sulphate, is shown conclusively by R. H. Smith, who varied the experiment by introducing the potassium sulphate after the ferric hydroxide precipitate had been formed, as well as before, and found the quantities carried down in both cases practically the same. A similar fact was shown in the case of aluminium hydroxide. In Series II facts similar to those just discussed for sulphur trioxide were noted in the case of chlorine. At no point were chlorine and potassium carried down at the same time. The proof for this is found in Series III, Experiments 22 and 23. At six molecules neither chlorine nor potassium are disturbed, but at five molecules 3.4 per cent. of the chlorine present appears in the precipitate and potassium is absent. From the preceding discussion it is evident that sulphur trioxide and chlorine can be carried down, in the given conditions, only as a resuit of the decomposition of potassium sulphate and potassium chloride respectively. This would imply with reference to ferric hydroxide, first, the power of decomposing either potassium sulphate or potassium chloride, as the case may be, and second, the power of selective combination.

Furthermore, this is emphasized by the results in Series III, where chlorine is undisturbed in the presence of potassium sulphate, although carried down when the latter is absent. These facts are certainly inconsistent with the theory

of adhesion or "mechanical inclusion," and, on the other hand, are characteristic of chemical action. As to the appearance of potassium in the precipitate at six and eight molecules in Series I, the evidence is not conclusive that it is the result of chemical action, but it suggests the formation of a salt of ferric hydroxide and potassium analogous to potassium aluminate, differing, however, from the latter in that it is insoluble.

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REVIEWS.

THE CONSTANTS OF NATURE. Part V. A RECALCULATION OF THE ATOMIC WEIGHTS. By FRANK WIGGLESWORTH CLARKE. Chief Chemist of the U. S. Geological Survey. New edition, revised and enlarged. The Smithsonian Institution. Washington. 1897. pp. 370.

The first edition of this now well known work appeared in 1882. A little later Meyer and Seubert published their book on "Atomic Weights," which was complete up to date. But the activity in the field of atomic weight determinations has been so great recently, that even the *Lehrbuch* of Ostwald, the second edition of which appeared in 1891, is by no means a complete record of what has been done up to the present. The appeareance of this new edition of Clarke's book is therefore timely.

The method which the author adopts in dealing with the results of the different experimenters, together with the reasons for its selection, will be seen best by examining a paragraph from the preface: "That all methods of averaging are open to objections, I am, of course, perfectly aware. I also know the doubts which attach to all questions of probable error, and to all combinations of data which depend upon them. I have, however, preferred to face these objections and to recognize these doubts rather than to adopt any arbitrary scheme which permits of a loose selection of data. After all, the use of probable error as a means of weighting, is but a means of weighting, and perhaps more justifiable than any other method of obtaining the same result. When observations are weighted empirically—that is, by individual judgment—far greater dangers arise. Almost unconsciously, the work of a famous man is given greater weight than that of some obscure chemist, although the latter may ultimately prove to be the best. But the probable error of a series of measurements is not affected by the glamor of great names, and the weight which it assigns to the observations is at least

as safe as any other. In the long run, I believe it assigns weight more accurately, and therefore I have trusted to its indications, not as if it were a mathematical fetich, but regarding it as a safe guide, even though sometimes fallible." That greater weight should *ceteris paribus* be attached to the use of simple methods than to those which are more complicated, is evident.

Further, that the separate determinations in any one series, made by exactly the same method, should agree with one another, is far less significant than that results by different methods, using different material, should agree. And, what appears to be most significant of all, is that different experimenters, working with different material, and with different methods, should obtain essentially the same result. It is on this ground that we now ascribe to oxygen the atomic weight 15.88, with a good deal of confidence.

But after all, it is but a matter of opinion as to the best method of dealing with results which do not agree closely with one another, in order to obtain the most probable value from them. Indeed, whatever opinion one may hold with respect to the method of assigning final values, this would scarcely affect the standing of this admirable book, for as Clarke states in his preface, "of course none of the results reached in this revision can be considered as final. Every one of them is liable to repeated corrections. To my mind the real value of the work, great or little, lies in another direction. The data have been brought together and reduced to common standards, and for each series of figures the probable errors have been determined. Thus far, however much my method of combination may be criticised, I feel that my labors will have been useful. The ground is cleared, in a measure, for future experimenters; it is possible to see more distinctly what remains to be done." And when we consider the amount and kind of work which has necessarily been spent in calculating upon a common basis all the atomic weight determinations which have ever been made, it is clear that Professor Clarke deserves high praise and the thanks of his brother chemists. H. C. J.

THE CHEMISTRY OF DAIRYING. An outline of the chemical and allied changes which take place in milk, and in the manufacture of butter and cheese; and the rational feeding of dairy stock. By HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Experiment Station. 156 pages. Easton, Pa.: Chemical Publishing Co. 1897.

This little book has been prepared from the author's lecture notes, and is designed for dairy students who have usually no knowledge of chemistry. While necessarily super-

ficial from a chemist's standpoint, the book affords interesting reading for any one who is seeking information in this line. Among the subjects treated are the following: Composition of milk, its products and by-products, milk testing, chemistry of butter and cheese making, sanitary questions of dairy, preserving milk, effects of food upon dairy products.

We notice some statements which do not appear to be in line with present knowledge. Thus, the author, on page 5, appears to confuse casein with the total nitrogen compounds. Albumin is used to include all nitrogen compounds exclusive of casein. It is stated that the "scum" which forms on boiled milk is albumin, while, in fact, it contains casein, sugar and fat as well, and is practically evaporated milk. Another instance is quoting Blyth to the effect that there is a constant ratio between the albumin and casein of normal milk. Blyth has been shown to be wrong in this, for the ratio varies greatly. Perhaps such errors in minor details do not detract from the practical value of the book for dairy students. In the main the book can be commended for its accuracy, clearness and comprehensiveness. L. L. V. S.

INORGANIC CHEMICAL PREPARATIONS. By FRANK HALL THORP, Ph.D., Instructor in Industrial Chemistry, Massachusetts Institute of Technology. Boston: Ginn & Co. 1896.

In the introduction to this book Dr. Thorp describes methods of work and apparatus. The book gives detailed methods for making a large number of salts; the instructions are clear and precise. Nearly all of the preparations are crystallized from aqueous solutions, giving an impression of monotony in the work. By adding to his list of salts some anhydrous halides, such as ferrous bromide and chloride, bismuth iodide, the chlorides of iodine, and some preparations requiring furnace work—for example, potassium cyanide, sodium sulphantimoniate, manganese, magnesium—the author could make his work more interesting. The more skillful students would thus be trained in manipulation which is quite within their power, but require more skill and practice than the preparations—with the exception of the anhydrous chlorides of aluminium and phosphorus—which are included in this book.

E. R.

TRAITE ELEMENTAIRE DE CHIMIE: (1) CHIMIE MINERALE, 366 pp.; (2) CHIMIE ORGANIQUE, 205 pp. PAR A. HALLER et P. TH. MULLER. Paris: Georges Carré, Éditeur. 1896.

These two volumes recall in size and arrangement Pinner's well-known "Repetitorien der Chemie," and doubtless will excellently serve the same purpose—that of preparing medical students, technical chemists, and pharmacists, for exam-

ination. The books are elementary, yet quite up to date. Such subjects as Raoult's methods of determining molecular weights, argon, carborundum, Moissan's furnace, carbides, pure hydroxylamine find mention in the first volume; the results of the late investigation of the sugars are included in the second. The presentation is very clear and compact; physical and stereo chemistry are not mentioned, but enough chemistry is given for those for whom the books are intended.

While the subject matter, printing, binding, and mechanical reproduction of the illustrations are thoroughly modern, the illustrations recall to the reviewer those happy days of youth, many years ago, when Stöckhardt's "Schule der Chemie" was a book in common use, and heating by gas was just introduced into laboratories. These illustrations recall those of Stöckhardt: the same picturesque charcoal-furnaces as source of heat; the same cork-stoppered U-tubes, serving as drying apparatus, and recalling the happy hours spent in making them air-tight; the same familiar open-top blast-furnace of fifty years ago. As historical and sentimental retrospect such pictures have value to a reviewer, but as a means of instruction to students their value is not great.

E. R.

THE PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. A manual for the examination of soils, fertilizers, and agricultural products. For the use of analysts, teachers, and students of agricultural chemistry. BY HARVEY W. WILEY, Chemist to the United States Department of Agriculture. Vol. II., FERTILIZERS. pp. vii, 322. Price, $2.00. Vol. III., AGRICULTURAL PRODUCTS. pp. xii, 666. Price, $3.75. Easton, Pa.: The Chemical Publishing Company.

The first volume of this work appeared about two years since and was noticed in this JOURNAL in December, 1895. The publication of the second and third volumes now rounds out a task for which the author has been well fitted, and which has been accomplished in a manner gratifying to chemists in general, and in particular to those dealing with agricultural materials and products. While treating primarily the analytical phase of the subject, the work will have a much broader application, and a distinct usefulness to the student of general chemistry.

The second volume is a presentation, as the author announces in the preface, of "a broad view of a great subject" and one which, so far as the writer has been informed, has not previously been attempted. The literature of fertilizer manufacture and analysis is scattered widely through technical and scientific journals, but has nowhere been so thoroughly compiled as in this volume. The fertilizer industry has from the first been subjected to rather rigid control by

state laws regarding the certified composition of all such materials offered for sale. In this respect, public opinion has been expressed more forcibly than in the case of any other agricultural material. The analysis of commercial fertilizers has, therefore, assumed official and legal dignity in most of the states, resulting in the organization of an Association of Official Chemists, and the adoption of official methods for conducting such analyses. From a long-standing connection with this Association, the author has attained a commanding view of the entire subject which is well reflected in this volume.

The discussion of the subject is a rational one, treating under separate heads of the three fertilizing elements of commercial importance, *viz.*, phosphorus, nitrogen and potassium, as regards their commercial occurrence, origin, and chemical estimation. A separate section is devoted to the analysis of miscellaneous materials of fertilizing value. The work is comprehensive, citing with great detail not only the analytical methods officially adopted in this and other countries where fertilizer control is exercised, but also giving place to the presentation of obscure and unimportant methods of purely scientific interest. Much useful information not strictly analytical, is also incorporated, as for instance upon the history, manufacture and characteristics of basic phosphatic slags; upon the chemistry of the manufacture of phosphates; and upon the production of the famous Stassfurt potash salts.

The third volume, treating of Agricultural Products, embraces of course, a much wider field and the discussion of methods concerning which less uniformity of opinion prevails than in many other branches of analytical chemistry. The first part devotes about fifty pages to sampling, drying, incineration and extractions, which certainly cannot be thought too much for these important operations. The detection and estimation of carbohydrates and the examination of products containing them are discussed in not less than 300 pages. This includes an excellent description of polarimetric instruments and the scientific principles involved in their use and construction. All of the best known optical, volumetric, and gravimetric methods for estimating carbohydrates are presented exhaustively. Attention is also given to the examination of crude materials like cane and beets for factory purposes, as well as the various sugar-factory products.

The estimation of fats and oils is discussed in a separate section in which all of the physical tests for these bodies are fully described. Of special interest is the section devoted to the separation and examination of the various nitrogenous bodies of both vegetable and animal origin, in which the re-

cent work of Osborne and his associates has been freely cited. The examination of dairy products, cereals, fodder, flesh, fruits, tea and coffee, tannin, tobacco, and fermented beverages are all amply discussed.

The estimation and calculation of the nutritive ratios and calorific values of food also receive due attention.

This enumeration may serve to show the comprehensive character of the work and, in a general way, its value. A closer examination will only strengthen the favorable opinion. The volumes are well bound and clearly printed on good paper. We are assured that the plates of the first edition have been destroyed, thus anticipating a revision for subsequent editions. There is little to criticise in the entire work and that only in regard to unimportant details. The whole is an exceedingly valuable contribution to chemical literature.

W. E. STONE.

VORLESUNGEN ÜBER BILDUNG UND SPALTUNG VON DOPPELSALZEN. By J. H. VAN 'T HOFF. 8vo. 95 pp. Leipzig: Engelmann.

This publication is a systematic summary of the previously published investigations made in the author's laboratory, on the conditions of equilibrium in which double salts are involved. The book is divided into three parts. The first part consists of a concise graphical and algebraic discussion of the theoretical principles involved, constituting probably the most valuable feature of the work; the second part describes the various methods of determining the transition temperature; and the third part treats of applications of the general principles to a number of special double salts. There can be no question of the great value of monographs of this kind, of which this distinguished author is peculiarly prolific, to the investigator and advanced student of theoretical chemistry.

A. A. N.

AN OUTLINE OF THE THEORY OF SOLUTIONS AND ITS RESULTS. For Chemists and Electricians. By J. Livingston R. Morgan, Ph.D., (Leipzig) Instructor in Quantitative Analysis, Polytechnic Institute, Brooklyn. John Wiley and Sons, New York. Chapman and Hall, London. 1897. pp. 63.

This little book deals with some of the fundamental ideas underlying the present theory of solutions, in an elementary way. The four chapters are on: The Theory of Solution, The Methods for Determining Electrolytic Dissociation, The Theory of the Voltaic Cell, and Analytical Chemistry from the Standpoint of Electrolytic Dissociation. It is stated in the preface that "if by this sketch the author can induce anyone to go deeper into the subject, he will feel more than repaid for his work."

H. C. J.